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Attenuation of Polybrominated Biphenyls and Hexachlorobenzene by Earth Materials

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ATTENUATION OF POLYBROMINATED BIPHENYLS AND HEXACHLOROBENZENE BY EARTH MATERIALS

by

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Amendment to
Grant No. R-804684-01

Project Officer

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16. ABSTRACT

The aqueous solubility, adsorption, mobility, and microbial degradation of polybrominate biphenyls (PBBs) and hexachlorobenzene (HCB) were studied under laboratory conditions. Studies indicated that PBBs were more than 200 times and HCB more than 2.5 times more soluble in landfill leachate than in distilled water. Also, the solubilities of PBBs and HCB were higher in creekwater and landfill leachates than in purified waters: this was correlated with a level of dissolved organics in the waters.

HCB showed a greater tendency for adsorption than did PBBs. There was a high direct correlation between the total organic carbon (TOC) content of soils and the amount adsorbed. PBBs and HCB were strongly adsorbed by the Ambersorb XE-348, but not so by organic solvents.

PBBs and HCB remained immobile when leached with water or landfill leachate but were highly mobile when leached with organic solvents. PBBs and HCB were found to be resistant to microbial degradation.

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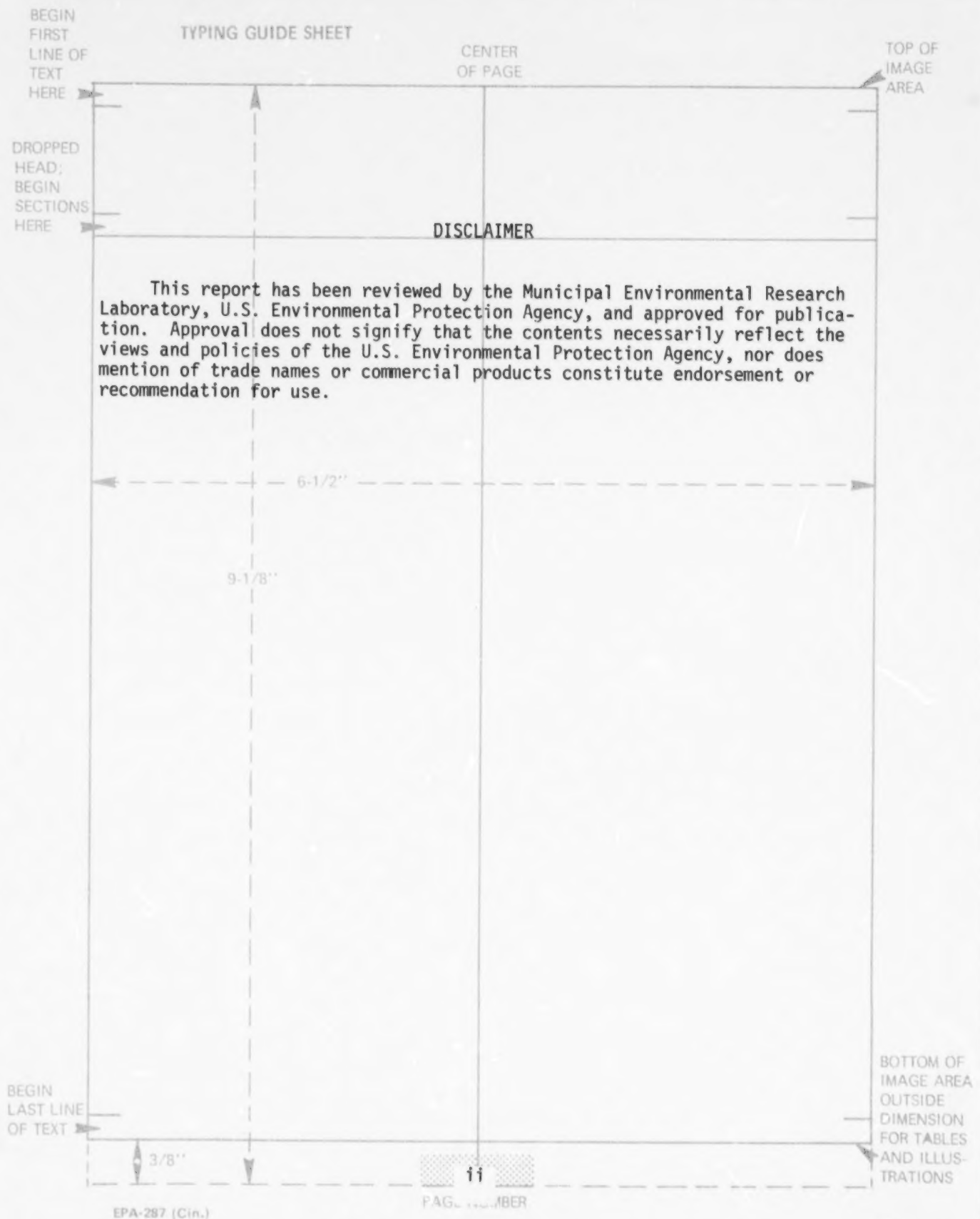
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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing concern of the public and government about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay among its components require a concentrated and integrated attack on the problem.

Research and development—those necessary first steps in solving a problem—involve defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new, improved technologies and systems to preserve and treat public drinking water supplies; to minimize the adverse economic, social, health, and aesthetic effects of pollution; and to prevent, treat, and manage waste water and solid and hazardous waste pollutant discharges from municipal and community sources. This publication is one of the products of that research; it is a vital communications link between the researcher and the community.

Results are reported from laboratory investigation of the capacity of earth materials to attenuate polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) from waters. These results are applicable to the design of treatment systems and earth material liners for sanitary landfills, and to the land disposal of municipal and hazardous wastes.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

The aqueous solubility, adsorption, mobility, and microbial degradation of polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) were studied under laboratory conditions. The solubilities of PBBs in two purified waters, a creek water, and two landfill leachates ranged from 0.06 µg/L in distilled water to 16.89 µg/L in landfill leachate. The solubility of HCB in the same waters ranged from 1.75 µg/L to 4.47 µg/L. PBBs were more than 200 times and HCB more than 2.5 times more soluble in landfill leachate than in distilled water. The solubilities of PBBs and HCB were higher in creek water and landfill leachates than in purified waters; this was directly correlated with the level of dissolved organics in the waters.

The adsorption of PBBs and HCB by soils and Ambersorb XE-348 carbonaceous adsorbent from aqueous solutions and organic solvents could be described by the Freundlich adsorption equation. HCB showed a greater tendency for adsorption than did PBBs. There was a high direct correlation between the total organic carbon (TOC) content of soils and the amount adsorbed. No measurable adsorption of either PBBs and HCB by soils occurred from organic solvents; however, they were strongly adsorbed by the Ambersorb from the solvents.

The mobilities of PBBs and HCB in five soils were measured with several leaching solvents using a soil thin-layer chromatography technique and column leaching studies. PBBs and HCB remained immobile in the soils when leached with water or landfill leachate but were highly mobile when leached with organic solvents. Mobility was directly proportional to the solubility of the compounds in the leaching solvents and to the soil organic matter content.

PBBs and HCB were found to be resistant to microbial degradation. Both compounds persisted, with no measurable degradation, in soils in experiments lasting 6 months and in solution culture experiments lasting 4 weeks.

This report was submitted in fulfillment of an amendment to Grant No. R-804684-01 by the Illinois State Geological Survey, University of Illinois, under partial sponsorship of the U.S. Environmental Protection Agency. Work was completed in October 1979.

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CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vi
Acknowledgment viii
1. Introduction 1
Manufacture and industrial uses 2
Chemical structure 2
Environmental effects 3
Disposal and soil attenuation 5
Degradation in the environment 6
Literature summary 7
2. Conclusions 8
3. Recommendations 10
4. Materials and methods 11
PBB and HCB materials 11
Adsorbents 11
Waters and leachates 12
Solubility studies 12
Instrumental parameters 14
Adsorption studies 15
Mobility studies 16
Microbial degradation studies 17
5. Solubility of PBBs and HCB in waters and leachates 20
Isomer identification 20
Quantitation 21
Solubility in pure waters 23
Solubility in waters and leachates 26
6. Adsorption of PBBs and HCB by soil materials and Ambersorb^{R} . . 29
Adsorption isotherm 29
Adsorption by soils 29
Adsorption of individual PBB isomers by soils 30
Effect of organic solvents on adsorption by soils 33
Adsorption by Ambersorb XE-348 from organic solvents . . . 33
Effect of soil TOC on adsorption 37
7. Mobility of PBBs and HCB in soil materials 39
Effect of leaching solvent and soil TOC 39
Column leaching studies 40
8. Degradation of PBBs and HCB in soil 42
Extraction of PBBs and HCB from soil 42
Soil incubation studies 43
References 46
Appendix: Publications related to this project 51

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FIGURES

Number		Page
1.	(A) Biphenyl structure; (B) hexachlorobenzene (HCB)	3
2.	Gas chromatogram of PBB isomers	20
3.	Gas chromatogram of the PBB mixture fireMaster BP-6	21
4.	Effect of pore size and number of continuative filtrations of 100-mL aliquots of HCB-saturated water on the concentration of HCB in filtrates	24
5.	Freundlich adsorption isotherms of PBBs on three soil materials from Blackwell leachate at 22°C	30
6.	Freundlich adsorption isotherms of ^{14}C-HCB on three soil materials from deionized water 22°C	30
7.	Gas chromatograms of PBBs remaining in Blackwell leachate	31
8.	Freundlich adsorption isotherms of PBBs and ^{14}C-PBBs adsorption on Ambersorb XE-348 from organic solvents at 22° ± 1°C	34
9.	Freundlich adsorption isotherms of HCB adsorption from several organic solvents on Ambersorb XE-348 at 22°C	34
10.	Freundlich adsorption isotherms of individual PBB isomers adsorbed by Ambersorb from hexane solution at 22°C	35
11.	Freundlich adsorption constant for PBBs plotted as a function of the organic matter content of soil	37
12.	Freundlich adsorption constant for HCB plotted as a function of the organic matter content of soil	38

TABLES

1.	Characteristics of soils used in adsorption and mobility studies	12
2.	Typical physical properties of Ambersorb XE-348	12
3.	Total organic carbon (TOC) and major elements analyses of waters used in PBBs and HCB solubility study	13
4.	Relative response of a ^{63}Ni electron capture detector to hexabromobenzene and PBB isomers	22
5.	Comparison of concentrations of PBB isomers determined by the internal standard (IS) technique	23

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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TABLES (continued)

Number		Page
6.	Distribution of PBB isomers in hexane- and water-soluble fractions of fireMaster BP-6, based on total area	25
7.	Solubility of the major isomers of PBBs in deionized water	25
8.	Solubility of HCB in deionized water	26
9.	Solubility of PBBs in waters and leachates (µg/L)	27
10.	Solubility of HCB in waters and leachates (µg/L)	28
11.	Freundlich parameters K (ng/g) and 1/n, and regression coefficient, r^2, for the adsorption of PBBs and ^{14}C-HCB on various soils from aqueous solution	29
12.	Quantitative distribution of major PBB isomers after adsorption by soils from Blackwell leachate	32
13.	^{14}C-PBBs and ^{14}C-HCB remaining in hexane solution after equilibrium with Catlin silt loam soil at 22° ± 1°C	33
14.	Freundlich parameters K (µg/g) and 1/n; regression coefficient, r^2; and melting point (M.P.), for the adsorption of ^{14}C-PBBs and ^{14}C-HCB from various organic solvents by Ambersorb XE-348	36
15.	Quantitative distribution of major PBB isomers remaining in solution after adsorption by Ambersorb XE-348 from hexane	36
16.	Mobility of PBBs and HCB in several soil materials leached with various solvents, measured by soil TLC	39
17.	Mobility of major PBB isomers in Catlin silt loam leached with acetone/water (1:1, v/v)	40
18.	Mobility of major PBB isomers in Catlin silt loam leached with acetone/water (8:2, v/v)	40
19.	Mobility of major PBB isomers in Catlin silt loam leached with acetone (100%)	41
20.	Percentages of ^{14}C-PBBs and ^{14}C-HCB recovered from soil columns leached with PBB- or HCB-ethanol solution	41
21.	Percentages of PBBs recovered from Catlin silt loam soil (3.33 ppm added by weight)	42
22.	Extraction of ^{14}C-HCB from soil using different solvents	43
23.	Recovery of PBB isomers after incubation of 10 ppm by weight in Catlin soil	44
24.	Percentage of HCB recovered after incubation of 3.33 ppm by weight in Catlin soil	45

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SECTION 1

INTRODUCTION

Polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) are both halogenated hydrocarbons that unfortunately have made their way into the environment. For instance, in 1973, PBBs were accidentally added to livestock feed in place of magnesium oxide. This incident had a catastrophic impact on the Michigan livestock industry and resulted in the killing of thousands of farm animals. The carcasses of these animals were disposed of by burial. Altogether approximately 29,800 cattle, 5,920 swine, 1,470 sheep, and 1.5 million chickens had been killed and buried by the end of 1975 (Carter, 1976; Isleib and Whitehead, 1975; Robertson and Chynoweth, 1975). This incident has been called the most costly and disastrous contamination to occur in United States agriculture (Isleib and Whitehead, 1975). The most tragic aspect, however, was the contamination of farm families who consumed products containing PBBs from their farms. The full consequences of these events will probably not be known for some time.

Hexachlorobenzene has been used as a seed dressing to prevent fungus disease in wheat. It is both a starting material and/or by-product of the chemical industry (Gilbertson and Reynolds, 1972). The present environmental concern is not over the use of HCB as a fungicidal seed treatment, but over the disposal of large quantities of HCB produced annually as a by-product of many manufacturing processes.

The purposes of the present study were: (a) to conduct a literature review of pertinent information on attenuation of PBBs and HCB in soil materials and their behavior in the environment; (b) to measure quantitatively the aqueous solubilities of PBBs and HCB and to determine the effect of increasing concentrations of dissolved organic matter (as found in river waters and landfill leachates) on the solubilities; (c) to measure the adsorption capacity of selected earth and carbonaceous materials for PBBs and HCB from aqueous and organic solvents; (d) to evaluate the effects of time, organic carbon content, adsorbent structure, and solvent on attenuation and mobility of PBBs and HCB; (e) to measure the persistence of PBBs and HCB to microbial degradation, both in solution cultures and soil; and (f) to use these data to develop a mathematical model that will allow prediction of PBB and HCB adsorption and mobility in earth materials. Data on the factors affecting PBB and HCB attenuation by earth materials would provide a useful basis for determining waste treatment methods, for predicting migration of these two compounds under landfills, and for selecting and designing future disposal sites.

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MANUFACTURE AND INDUSTRIAL USES

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Polybrominated biphenyls

The commercial production of PBBs began in 1970. Approximately 13.3 million pounds of PBBs were produced in the United States from 1970 to 1976 (Neufeld, Sittenfield, and Wolk, 1977). About 11.8 million pounds of this total was hexabromobiphenyl marketed under the names of fireMaster BP-6 or FF-1; the remaining 1.5 million pounds consisted of octabromobiphenyl (OBB) and decabromobiphenyl (DBB). Michigan Chemical Corp. (St. Louis, Michigan) produced BP-6, and White Chemical Co. (Bayonne, New Jersey) and Hexcel Corp. (Sayreville, New Jersey) manufactured octabromobiphenyl and decabromobiphenyl. Michigan Chemical Corp. discontinued BP-6 production in 1974, and White Chemical Co. and Hexcel Corp. discontinued their OBB and DBB production in early 1977 (Di Carlo, Seifter, and De Carlo, 1978).

At present, no PBBs are being imported in commercial quantities. On the other hand, the export of PBBs from the United States to Europe has increased during the past several years, and totaled 805,000 pounds in 1976 (Neufeld, Sittenfield, and Wolk, 1977). The major uses of PBBs were for the production of flame retardant resins of acrylonitrile, bertadiene, and styrene for business machines, electrical housings, textiles, and other materials (Sundström, Hutzinger, and Safe, 1976; Di Carlo, Seifter, and De Carlo, 1978). All of these uses were discontinued in late 1974 as a result of the Michigan incident (Di Carlo, Seifter, and De Carlo, 1978).

Hexachlorobenzene

HCB is both a starting material and by-product of the chemical industry (Gilbertson and Reynolds, 1972). The two major uses of HCB in industry are as a peptizing agent in the manufacture of styrene and nitroso rubbers for tires, and as a grain fungicide for seed treatment (Quinlivan, Ghassemi, and Santy, 1975).

Quinlivan, Ghassemi, and Santy (1975) estimated that 3,090 metric tons of HCB was generated annually in the United States, of which approximately 240 metric tons were used in the manufacturing of tires, and/or in seed treatment. The rest was produced as by-product waste and is disposed of primarily on land or by incineration. HCB is present in industrial waste as a by-product in several manufacturing processes, mainly in the commercial production of various chlorinated solvents such as carbon tetrachloride, perchloroethylene, dichloroethylene, and trichloroethylene. HCB has also been present as an impurity or by-product in the production of several pesticides such as dacthal, mirex, simazine, atrazine, propazine, and pentachloronitrobenzene (Quinlivan, Ghassemi, and Santy, 1975).

CHEMICAL STRUCTURE

PBBs and HCB belong to a class of aromatic halogenated organic compounds. PBBs are chemically similar to the more commonly known contaminants, polychlorinated biphenyls (PCBs) and polychlorinated naphthalene (PCN). The

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term polybrominated biphenyls refers to a group of chemicals that is formed by substituting bromine for hydrogen in the biphenyl structure. Although theoretically 209 brominated biphenyls are possible, only about 40 have actually been synthesized in pure form, even on a laboratory scale (Sundström, Hutzinger, and Safe, 1976). There are more than 30 different isomers in fireMaster PB-6 that have been separated in our laboratory by using an SE-30 glass capillary gas-chromatographic column. Jacobs, Chou, and Tiedje (1976) found that 18 different components were detected in commercial fireMaster BP-6. The quantity of each isomer varies somewhat with each batch, but a hexabromobiphenyl isomer was always the largest and a heptabromobiphenyl isomer the second largest component in the fireMaster BP-6 or FF-1. Both fireMaster BP-6 and FF-1 have an average bromine content equivalent to 6 bromine atoms per molecule.

HCB is formed by substituting chlorine atoms for all the hydrogen atoms in the benzene ring. The basic biphenyl and HCB structures are shown in figure 1.

ENVIRONMENTAL EFFECTS

Polybrominated biphenyls

PBBs are structurally similar to PCBs, a well-known environmental pollutant (Griffin and Chian, 1979); however, PBBs received little attention from chemists and biologists before the PBB incident that occurred in Michigan in 1973 (Carter, 1976; Jackson and Halbert, 1974; Isleib and Whitehead, 1975; Robertson and Chynoweth, 1975). Tragically, farm families were also contaminated by eating food products (such as milk and garden vegetables) from their farms that contained PBBs. The full consequences of this PBB contamination will probably not be known for some time. According to an investigation of 298 persons exposed to contaminated products as a result of this incident, concentrations of PBBs were found in their blood, milk, and adipose tissue in amounts up to 2.26, 92.66, and 174.0 ppm respectively (Humphrey and Hayner, 1975). Subsequent studies in Michigan have shown that PBBs can cause liver, kidney, and brain damage in animals, and liver damage and personality changes in humans (Moorhead, Willett, and Schanbacher, 1978; Schanbacher et al., 1978; McCormack et al., 1978; Anderson et al., 1978a, 1978b).

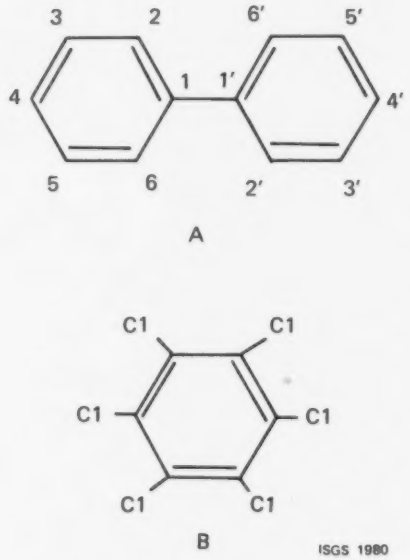

Figure 1. (A) Biphenyl structure: positions 2 to 6 and 2′ to 6′ indicate possible positions for bromine substitution to form polybrominated biphenyls (PBBs); (B) hexachlorobenzene (HCB).

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Because PBBs are fat soluble and poorly metabolized, they have entered the food chain and accumulated in adipose tissues of fish, ducks, and mammals, including humans (Hesse and Powers, 1978; Robl et al., 1978; Humphrey and Hayner, 1975; Isbister, 1977). Hesse and Powers (1978) have shown that PBBs accumulated in the tissue of a caged fish (1000 µg/kg) in Pine River, where water concentrations of PBBs remained consistently less than 0.1 µg/L. The PBB bioaccumulation factor was greater than 10,000-fold as a result of 2 weeks exposure. Bioaccumulation of PBBs, therefore, appears comparable to that of PCBs: Hansen et al. (1971) reported PCB bioaccumulation factors in two fish species to be 10,000 to 50,000 times the exposure levels in water.

According to the monitoring studies of the Pine River water, Hesse and Powers (1978) found detectable concentrations of PBBs (in a range of 0.01 to 0.07 µg/L) downstream from the Michigan Chemical Corp. plant as far as 12 miles below the city of St. Louis, Michigan, in August 1974. In a more localized sampling of sediments near the Michigan Chemical Corp. plant, outfalls of PBB concentrations in nearshore sediments were as high as 77 ppm.

In another investigation, Shah (1978) noted that trace levels of PBBs were detected in ground-water samples from an aquifer that adjoined the Gratiot County landfill, located near St. Louis, Michigan. This landfill had received 269,000 pounds of wastes containing 60 to 70 percent PBBs between 1971 and 1973. The US-EPA has also found residues of PBBs elsewhere in the United States (Dayton Daily News, August 4, 1977; Di Carlo, Seifter, and De Carlo, 1978).

Hexachlorobenzene

Mismanagement of HCB-containing wastes has resulted in several episodes of environmental contamination in the United States and abroad. The best documented case of HCB contamination occurred in southern Louisiana, where in December 1972, the U.S. Department of Agriculture (USDA) reported the detection of HCB in cattle near Darrow, Louisiana (Booth and McDowell, 1975; Burns and Miller, 1975). Quarantine restrictions were imposed in that region, which involved approximately 120 square miles and about 20,000 cattle. The occurrence and effects of HCB have been reported in many organisms such as birds (Vos et al., 1971; Cromartie et al., 1975), rats (Medline et al., 1973), fish (Holden, 1970; Johnson, Stalling, and Hogan, 1974; Zitko, 1971), sheep (Avrahami and Steele, 1972), and man (Cam and Nigogosyan, 1963).

Laseter et al. (1976) reported that HCB concentrations reached a maximum of 88 µg/g (ppm) in bass following 15 days of exposure to 2 ppb in the water. Bioaccumulation factors in excess of 44,000-fold were found, with the highest level being 100,000-fold. They also noted that some changes were observed in kidney, liver, and gall bladders of bass exposed to 25 ppb HCB.

By 1974, the USDA had identified HCB in domestic meat and poultry supplies in at least 14 states. The livestock in several of these states were found to contain HCB residues above the acceptable level of 0.5 ppm (Booth and McDowell, 1975).

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The major problem with PBB and HCB intake by man is that he resides at the top of most food chains; therefore, he can take in substantial amounts of PBBs and HCB even if only trace levels are present at the bottom of the food chain—in the waters of streams, lakes, and/or in meat.

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DISPOSAL AND SOIL ATTENUATION

Polybrominated biphenyls

There is little information on the disposal of PBB wastes in scientific literature, except for that concerning the Gratiot County landfill near St. Louis, Michigan, and the disposal site in Kalkaska County, Michigan, where PBB-contaminated animals were buried. Shah (1978) estimated that approximately 161,400 to 188,300 pounds of PBBs had been deposited in the Gratiot County landfill, and 100 pounds of PBBs had been deposited in all the buried carcasses in the Kalkaska site.

The hydrophobic characteristic of PBBs makes them easily adsorbed from aqueous solution onto soils, with the amount adsorbed depending on the soil texture and organic carbon content, according to Filonow, Jacobs, and Mortland (1976). They found a linear correlation between adsorption capacity and total organic carbon content of the soil. The PBBs were extremely persistent, and no isomer showed any consistent decrease in concentration in soil incubations of up to one year (Jacobs, Chou, and Tiedje, 1978). In a separate study of PBB uptake by three root crops (radishes, carrots, and onions) in two soils, Chou et al. (1978) found that the extent of PBBs associated with the roots from the high-PBB treatment soil (100 ppm) ranged from approximately 50 to 500 ng/g plant tissue for plants grown in low-clay and low organic matter soil, and ranged from 30 to 120 ng/g plant tissue for plants grown in high-clay and high organic matter soil. Although some root crops from highly contaminated soil might contain traces of PBBs, much of the contamination could apparently be removed by peeling.

Filonow, Jacobs, and Mortland (1976) percolated water through soil columns containing 100 ppm of the PBB isomer hexabromobiphenyl. They found less than 0.6 percent of the hexabromo isomer was lost from each soil, even with leachate quantities equivalent to 20 times the average annual rainfall in Michigan.

Incineration is considered the safest method for disposal of PBB wastes. Destroying the PBB-contaminated cattle in Michigan by incineration was considered, but the facilities for such an action were not available when the incident occurred. It is extremely costly to build an incinerator; besides the cost, there are other difficulties connected with the incineration of PBB wastes. PBBs are structurally similar to PCBs, and the problems with PCB incineration have been documented previously (Duvall and Rubey, 1977; Moon, Leighton, and Huebner, 1976). Like PCBs, PBBs do not burn readily and incinerating conditions must be carefully controlled; otherwise, these compounds will reenter the environment in the stack gases. Land burial or landfill—much less expensive, accessible, and more energy efficient than incineration—is thus a desirable alternative for PBB disposal.

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Hexachlorobenzene

One problem of HCB disposal involves the high costs and fees for transporting hazardous wastes to regional incinerators or approved landfills. The costs for disposal at sites that specially treat or incinerate HCB wastes are much higher than the costs for land disposal (Quinlivan, Ghassemi, and Santy, 1975). Based on a survey by Quinlivan and his co-workers, methods currently used for the disposal of HCB-containing wastes include land disposal (sanitary landfill, industrial landfill, deep well injection, and dry pond), incineration, open pit burning, resource recovery, discarding into municipal sewage treatment plants, and emission to the atmosphere.

Quinlivan, Ghassemi, and Santy (1975) also noted that the major problem with disposal of HCB into sanitary or industrial landfills was vapor phase transport, due to the volatility of the compound. It was determined, however, that landfill disposal can be environmentally acceptable if an adequate soil cover, which may include an intermediate layer of plastic, is provided, and if the geology of the site is suitable for waste and leachate contaminants.

Farmer, Yang, and Letey (1977) discovered that highly compacted wet soil covers are most effective in reducing HCB volatilization. They also noted that other soil parameters such as soil organic matter content and soil texture, which may affect the extent to which HCB is adsorbed by soil, affect the rate of volatilization but not its magnitude. The Louisiana Air Control Commission (1973) reported that soil and plant samples taken from near landfill areas used for disposal of HCB wastes showed decreasing amounts of HCB as distance from the landfill increased. Burns and Miller (1975) reported high levels of HCB in the plasma of landfill workers handling hexachlorobenzene wastes. The levels ranged from 2 to 345 ppb of HCB in the plasma. At present there is no information to indicate that significant microbial degradation of HCB occurs in the environment.

DEGRADATION IN THE ENVIRONMENT

Polybrominated biphenyls and hexachlorobenzene are extremely persistent in soils. No evidence of significant microbial degradation of PBBs was found in soil incubation studies (Jacobs, Chou, and Tiedje, 1976; 1978). PBBs are very sensitive to UV-light, however. Ruzo and Zabik (1975) found that lower brominated biphenyls formed when PBBs were irradiated by UV-light. Similar findings were also reported by Anderson et al. (1975). They reported that the degradation of hexabromobiphenyl was much more rapid than a hexachloro analog; less than 10 percent of the initial compound persisted after 9 minutes of illumination. At present, there is no information to indicate that biological degradation of PBBs occurs in animals.

In laboratory studies, Beck and Hansen (1974) found that HCB was highly persistent in soil. The half-life of HCB in soil under controlled conditions was approximately 4 years. Isensee et al. (1976) also noted that no soil-incorporated HCB was lost under aerobic (sterile and nonsterile) and anaerobic nonsterile conditions for 1 year. Photodegradation was observed when HCB was irradiated by UV-light. Laseter et al. (1976) found that less than

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10 percent of the original HCB remained after 60 minutes of irradiation in benzene. Mehendale, Fields, and Matthews (1975) observed dechlorination of HCB in rat microsomal enzyme. Through in-vitro studies, they reported that pentachlorophenol was formed by adding the co-enzyme NADPH into the system.

LITERATURE SUMMARY

The information available at present indicates that PBBs and HCB are persistent in and have a strong affinity for soil, and that the nature of the soil and the organic matter content are factors affecting adsorption. Quantitative data on the adsorption capacities and factors affecting PBB and HCB adsorption by soils are lacking; yet they are needed to assess the impact of soil attenuation mechanisms on restricting PBB and HCB mobility in the environment.

Little information exists on the aqueous solubilities of PBBs and HCB under well-defined conditions. The present data suggest that increasing levels of dissolved organic matter increase the aqueous solubility of PBBs. This could have an important effect on the mobilities of both PBBs and HCB in soil environments where high organic leachates from sanitary landfills are percolating.

Apparently, PBBs are not transported in the environment through volatilization because of their low vapor pressures. The present information concerning HCB, however, suggests that because of its moderate vapor pressure and its subsequent volatilization, an important pathway for HCB transport in the environment is vapor phase migration through soil pores.

The available data are inadequate to assess the aqueous solubilities or adsorption mechanisms and capacities of earth meterials for PBBs and HCB. More data on the factors affecting PBB and HCB attenuation by earth materials are necessary to help make predictions about the fate and transport of these compounds in the environment.

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SECTION 2

CONCLUSIONS

Studies of the aqueous solubility, adsorption, mobility, and microbial degradation of PBBs and HCB have led to the following conclusions:

1. The PBB material known as fireMaster PB-6 is a mixture of more than 30 isomers. The six major isomers are 2,2',4,5,5'-penta-; 2,3',4,4',5'-penta-; 2,2',4,4',5,5'-hexa-; 2,2',3,4,4',5'-hexa-; 2,3',4,4',5,5'-hexa-; and 2,2',3,4,4',5,5'-heptabrominated biphenyl.

2. The water-soluble fraction of PBBs was richer in the lower brominated isomers than in the hexane-soluble material.

3. Both PBBs and HCB reached saturation concentrations in water in less than 2 days.

4. Filter pore size was a major factor in the measurement of the aqueous solubility of PBBs and HCB. It is recognized that the definition of solubility in this study is basically an operational one, using pre-saturated 0.22-μm pore size membranes as the basis for the solubility values reported.

5. The solubilities of PBBs in distilled water, deionized water, creek water, Du Page leachate, and Blackwell leachate were 0.057 μg/L, 0.317 μg/L, 0.497 μg/L, 8.889 μg/L, and 16.892 μg/L, respectively; the solubilities of HCB in the same waters and leachates were 1.75 μg/L, 1.78 μg/L, 2.22 μg/L, 4.14 μg/L, and 4.47 μg/L, respectively.

6. PBBs were more than 200 times more soluble and HCB more than 2.5 times more soluble in landfill leachate than in distilled water.

7. The solubilities of PBBs and HCB were higher in creek water and landfill leachates than in purified waters; this was directly correlated with the level of dissolved organics in the waters.

8. The adsorption of PBBs and HCB by soils and Ambersorb XE-348 from aqueous solutions and organic solvents could be described by the Freundlich adsorption equation. All regression coefficients (r^2) were greater than 0.98.

9. HCB had a greater tendency for adsorption under these experimental conditions than did PBBs. The adsorption of PBBs and HCB on three soils followed the series: muck > Catlin > Ava.

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10. There was a high direct correlation between the total organic carbon (TOC) content of the soil and the amount adsorbed.

11. Preferential adsorption of individual PBB isomers was noted and found to depend on the characteristics of the adsorbent.

12. Little or no adsorption of either HCB or PBBs by soils was found from hexane or ethanol solutions.

13. PBBs and HCB were strongly adsorbed from organic solvents by Ambersorb XE-348. There were substantial differences in adsorption among the four organic solvents tested. The polarity and steric effects of both solvent and solute appear to be important factors in the amounts of PBBs and HCB adsorbed. Carbonaceous adsorbents may be suitable for waste treatment or as waste pit liners where it is desired to adsorb PBBs or HCB from organic solvents.

14. PBBs and HCB remained immobile in the soils when leached with water or landfill leachate, but were highly mobile when leached with organic solvents. Mobility was proportional to the solubility of the compounds in the leaching solvents and to the soil organic matter content.

15. These results indicate it may not be feasible to dispose of PBBs and HCB dissolved in organic solvents in soils. Migration in a landfill environment could occur if PBB or HCB wastes dissolved in organic solvents, or if organic solvents together with PBB or HCB wastes were disposed of in the same location.

16. PBBs and HCB persisted for 6 months in soil with no significant microbial degradation.

17. Since PBBs are not degraded, are not leached by water, are not taken up by plants, and are not readily volatilized (because of their low vapor pressure), we expect PBBs to be a permanent component of contaminated soils. The same conclusions are probably true for HCB if the wastes are buried with a wet compacted cover soil to prevent migration in the vapor phase due to volatilization.

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SECTION 3

RECOMMENDATIONS

The results of our study document how organic solvents increase the mobility of PBBs and HCB, and how carbonaceous adsorbents such as Ambersorb XE-348 are capable of adsorbing PBBs and HCB from organic solvents. These findings led to our recommendation that PBB or HCB wastes dissolved in organic solvents and/or co-disposal of PBB and HCB materials with organic solvents be avoided at land disposal sites unless a carbonaceous liner material is used.

Because it was shown that adsorption of PBBs and HCB by soils was essentially zero in organic solvents, the problem of predicting PBB and HCB migration shifted from adsorption to fluid conductivity. Prediction of migration depends on a knowledge of what the fluid conductivity of the soil material is to the organic solvent. Unfortunately, information on this subject is sparse. To predict migration, more information is needed to determine the effects of soil properties, soil moisture conditions, and organic solvent interactions on the migration rate of the solvent through soil materials in a landfill environment.

The results and conclusions formulated from this study deal specifically with attenuation and mobility of PBBs and HCB in the liquid phase. Vapor phase transport through soil pores was ignored; however, for compounds with a moderate or high vapor pressure, such as HCB, this means of migration may be a significant mechanism for redistribution. More information is needed to assess the magnitude of this means of migration for organic wastes.

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SECTION 4

MATERIALS AND METHODS

PBB AND HCB MATERIALS

The Michigan Chemical Corp. supplied fireMaster BP-6 (lot #6244A); it was used without further purification.

^{14}C-PBBs (lot #872-244) were synthesized and purified according to our specifications by New England Nuclear Corporation, Boston, Massachusetts. The product contained the two major isomers of fireMaster BP-6: approximately 65 percent 2,2',4,4',5,5'-hexabromobiphenyl, and 35 percent 2,2',3,4,4',5,5'-heptabromobiphenyl. Identity was confirmed by finding retention times identical to standards run on Dexsil 300 and SE-30 gas chromatographic columns. No other components were detected by gas chromatography. The specific activity of ^{14}C-PBBs was 9.34 mCi/mmole.

Hexachlorobenzene (HCB) was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. The product was recrystallized from glass-distilled hexane. This process was repeated several times until the purity reached nearly 100 percent.

^{14}C-HCB (lot #852-058) was purchased from New England Nuclear Corporation, Boston, Massachusetts. The specific activity was 35.5 mCi/mmole, (0.125 mCi/mg). No other components were detected by gas chromatography.

ADSORBENTS

The adsorbents used in the adsorption study were Catlin silt loam soil (CS), Ava silty clay loam soil (AS), Houghton muck soil (HMS), and Ambersorb XE-348 (a carbonaceous adsorbent, Rohm and Haas, Philadelphia, Pennsylvania). The physical characteristics of the three soils are presented in table 1. The methods of analysis have been described by Griffin and Shimp (1978). The Ambersorb XE-348 was selected for the study because of its potentially high adsorption capacity for PBBs and HCB from organic solvents; its physical properties are shown in table 2. All the soil materials were ground in a mortar with pestle and screened (100 mesh) before use.

In the mobility studies, Catlin silt loam soil, Flanagan silty clay loam soil, Ava silty clay loam soil, Bloomfield loamy sand, and Ottawa silica sand were used as adsorbents. Their physical characteristics are also presented in table 1. These soil materials were also ground in a mortar with pestle and screened through a 28 mesh sieve before use.

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TABLE 1. CHARACTERISTICS OF SOILS USED IN ADSORPTION AND MOBILITY STUDIES

Soils	pH	CEC (meq/100 g)	Surface area* (m^2/g)	Sand	Silt	Clay	Organic carbon (%)
Catlin silt loam	7.1	18.1	130	6.1	61.4	32.5	4.73
Ava silty clay loam	4.5	13.1	125	1.1	64.3	34.6	1.18
Houghton muck	7.2	72.4	425	15.7	50.8	33.5	16.81
Flanagan silty clay loam	6.6	23.3	93	5.4	65.2	29.4	2.62
Bloomfield loamy sand	5.7	0.8	2	82.0	10.0	8.0	0.21
Ottawa silica sand	5.2	0.0	<1	100.0	0.0	0.0	<0.01

*Ethylene glycol method of Bower and Gschwend (1952).
CEC = Cation exchange capacity.

WATERS AND LEACHATES

Distilled water, deionized water, Sugar Creek water, Blackwell leachate, and Du Page leachate were selected for use in the solubility study. Leachates were centrifuged in a continuous flow centrifugation apparatus (Model JCF-Z, Beckman Instruments) at approximately 17,000 rpm prior to passing through a 0.22-µm pore size Millipore^R cellulose acetate membrane. Sugar Creek water was also passed through the 0.22-µm pore size membrane before use. The total organic carbon (TOC) and chemical analysis of the waters and leachates are shown in table 3.

SOLUBILITY STUDIES

A 3-g aliquot of either fireMaster BP-6 or hexachlorobenzene (HCB) was placed in a 5-gallon glass carboy, which had been cleaned, then baked at 450°C overnight. The carboy was filled with deionized water that had passed through a Milli-Q Reagent grade water system (Millipore Corp., Bedford, Massachusetts), then sealed with an aluminum-wrapped rubber stopper and wrapped with aluminum foil and masking tape to protect it from exposure to light. The solution in the carboy was agitated vigorously with a magnetic stirring bar coated with Teflon. Water samples were collected from the carboys after 6 months and 1 year and aliquots of the PBB- or HCB-saturated water solution were filtered separately through a variety of filter materials to determine the effects of filter composition and pore size on solubility results. The filter materials investigated were 0.7-µm pore size glass microfiber filters

TABLE 2. TYPICAL PHYSICAL PROPERTIES OF AMBERSORB XE-348*

Appearance	Black, spherical, non-dusting
Total surface area (N_2, BET method) (m^2/g)	500
Bulk density (g/cm^3)	0.60
Pore volume (cm^3/g)	0.58
Particle size (U.S. sieve series)	20-50
Crush strength (kg/particle)	1.0
Ash content (%)	<0.5

*Reported by Rohm and Haas (1977).

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TABLE 3. TOTAL ORGANIC CARBON (TOC) AND MAJOR ELEMENTS ANALYSES OF WATERS USED IN PBBs AND HCB SOLUBILITY STUDY

Waters	TOC (ppb)	B (mg/L)	Ca (mg/L)	Cr (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Zn (mg/L)	Na (mg/L)	K (mg/L)
Distilled water	335	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Deionized water	336	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Sugar Creek	1,841	0.083	80.4	0.013	0.014	28.3	BDL	0.087	10.1	1.8
Blackwell leachate	63,030	0.915	48.3	0.133	0.135	191.0	0.045	0.087	291.0	232.0
Du Page leachate	83,690	2.690	33.6	0.092	0.191	140.0	BDL	0.271	321.0	281.0

BDL = Below detection limit.

(Whatman, Inc., Clifton, New Jersey); glass wool plugs tightly packed into the stems of glass funnels; Millipore cellulose acetate membranes (0.22 and 0.45 µm); and Teflon membranes (0.5 µm, Millipore Co., Bedford, Massachusetts). PBB or HCB water solutions in 1-L quantities were passed through each of the membranes or filters to saturate the adsorption sites before the samples used for analysis were passed through the membranes or filters. The initial liter of each of the filtrates was discarded into a waste container. Prior experiments had shown that 1 liter was sufficient to saturate each of the membrane's adsorption capacities.

Subsequent experiments showed that it was more convenient to presaturate the membranes than to pass a liter of solution through them. This was accomplished by soaking the membranes in 300 mL of PBB- or HCB-saturated water, which was changed each day for 3 days. The membranes were then washed with deionized water, and 200 mL of PBB- or HCB-saturated water was flushed through the membrane by application of a vacuum to the filtration apparatus. A vacuum was not applied to glass microfiber filters or glass wool plugs because their filtration rate was fast and did not require vacuum assistance. The flushing filtrate was discarded and the sample was filtered. This second filtrate was then extracted for subsequent analysis.

A 100-mL aliquot of each of the filtrates was placed into a 250-mL separatory funnel and then extracted three times with 10-, 5-, and 5-mL portions of water-saturated hexane. Then 5 mL of 50 percent w/v sodium hydroxide and 0.5 mL of ethanol were added to each separatory funnel to break any emulsion that might have formed. This was followed by addition of 10 mL of the aqueous phase back into the separatory funnel to remove residual ethanol from the hexane. Breaking the emulsion in this manner was especially important during extraction of the leachates.

The three portions of extract were combined and a small amount of anhydrous sodium sulfate was added to remove excess water. An internal standard consisting of 0.25 µg of hexabromobenzene was added to the PBB extracts, and 0.25 µg of tribromobenzene was added to the HCB extracts. All the extracts were then concentrated to 1.0 mL using a Kuderna-Danish (K-D) concentrator in a water bath (at approximately 90°C).

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The extraction efficiency was checked by adding aliquots of 0.25 µg and 0.5 µg of PBBs, as well as 0.1 µg and 0.25 µg of HCB respectively, into four flasks containing 100 mL of deionized water, and extracted in the same manner as previously described. The extraction efficiency was also checked by adding ^{14}C-labeled PBBs and HCB into 100 mL of deionized water at four different concentration levels. The percentage of recovery of spiked and ^{14}C-PBBs and ^{14}C-HCB ranged from 98 to 101 percent.

In a separate solubility study of PBBs and HCB in waters and leachates, a 0.5-g and a 0.1-g aliquot of fireMaster BP-6 and HCB respectively were placed in 1-L Erlenmeyer flasks, then filled with either distilled water, deionized water, Sugar Creek water, Du Page leachate, or Blackwell leachate. The solution in the Erlenmeyer flask was agitated with a magnetic stirring bar in the same manner as previously described. Water samples were collected after 2, 4, and 7 days for PBBs and 2, 7, and 30 days for HCB. Aliquots of 250 mL of PBB and HCB water solutions were filtered through PBB- and HCB-saturated Millipore membranes (0.22 µm). Two 100-mL filtrates were then extracted with water-saturated hexane. The membrane saturation and extraction procedures followed in the same manner as described previously.

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INSTRUMENTAL PARAMETERS

The concentrated PBB and HCB extracts were analyzed on a Perkin-Elmer Sigma I gas chromatograph equipped with either an electron capture detector (ECD) or a flame ionization detector (FID). The conditions for the gas chromatographic analysis for PBBs and HCB were as follows:

	PBBs		HCB
Column	6-ft x 2-mm I.D. glass column, 3% SE-30 on 80/100 mesh Chromosorb WHP	48-m SE-30 WCOT capillary column (0.5 mm I.D.) 1:30 split ratio	6-ft x 2-mm I.D. glass column, 5% OV-17 on 80/100 mesh Chromosorb WHP
Injection port temperature	270°C	280°C	250°C
Column temperature	250°C	270°C	200°C
Detector temperature	300°C	300°C	300°C
Carrier gas	Methane/argon, flow 40 mL/min	Methane/argon, flow 2.7 mL/min	Methane/argon, flow 35 mL/min

A PBB mixture contains a variety of isomers and it was not possible to obtain them all for quantitation in this study; therefore, the relative response of each isomer to the internal standard was used for quantitation. In this case, the linear response of the FID to the various PBB isomers was used to help calibrate the ECD to the PBB isomers. When FID was used, the instrumental parameters were those given for the packed column.

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An assumption was made that all of the isomers of fireMaster BP-6 gave the same FID response; then the percentage of each isomer was calculated from known concentrations. Based on the known concentrations of each isomer and the response factors determined for the ECD, it was possible to calculate the isomer concentrations in unknown samples.

Since HCB does not contain isomers with different degrees of chlorination, the quantitation of HCB using the ECD was readily accomplished using the internal standard technique. This method, using HCB standards of 0.03 ppm and 0.05 ppm, consistently yielded percentages of error that were less than 1 percent.

Mass-spectrometer analyses of samples were carried out on a contract basis by the Institute for Environmental Studies, University of Illinois. The component identification was achieved by injection of extracts into a SE-30, 30-m glass capillary column. The instrument used was a Hewlett-Packard 5985A GC/MS/data system. The data system is then capable of searching the resident mass-spectral libraries to identify the number of bromine atoms on each of the isomers.

ADSORPTION STUDIES

All glassware was cleaned by soaking in soap and water, rinsing with tap water, rinsing with deionized water, rinsing again with reagent grade acetone, then baking in an oven at 450°C for at least 8 hours. The adsorption studies were carried out by placing weighed amounts of adsorbent into 125-mL serum bottles.

PBB-saturated Blackwell leachate and ^{14}C-HCB-saturated water were obtained by taking aliquots of the leachate and water and filtering the solutions through PBB- and HCB-saturated Millipore membranes (0.22 μm). Volumes of PBB and HCB filtrate, in 100-mL and 50-mL amounts respectively, were then added to each of the serum bottles containing the adsorbent. The bottles were sealed with a sheet of aluminum foil followed by a Teflon-coated septum and a crimp cap (Pierce Chemical Company, Rockford, Illinois). The bottles were then shaken overnight in a water bath at 22 ± 0.5°C.

The bottles were removed from the shaker and placed directly into a Model JS-7.5 rotor and centrifuged at a constant temperature of 22 ± 1°C in a Beckman Model J-21B centrifuge for 10 minutes at 4000 rpm. The bottles were then removed from the centrifuge head, the seals broken, and either 1 mL of the clear supernatants were pipetted for total ^{14}C-HCB count, or a 75-mL aliquot was extracted with water-saturated hexane for PBB analysis. The extraction and analytical procedures followed were the same as previously described. The ^{14}C was assayed by liquid scintillation counting. One mL of supernatant or organic solvent was counted in 10 mL of Bray's solution (Bray, 1960). All counts were corrected for quenching and machine efficiency.

In a separate study, weighed amounts of soils and Ambersorb XE-348 were placed into 125-mL serum bottles. Twenty-five-mL aliquots of ^{14}C-PBBs

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or ^{14}C-HCB dissolved in one of several organic solvents (ethanol, hexane, ethyl acetate, and ethylene dichloride) were added to the reaction bottles. In order to determine the isomer distribution after reaction of PBBs and Ambersorb XE-348, aliquots of 25 mL of hexane-soluble non-^{14}C-PBBs were also used. The bottles were treated in the same manner as described previously, except centrifugation was unnecessary, and gravity separation of solid from liquid was used.

The effect of reaction time on PBB and HCB adsorption was studied using these same methods. Two series of samples were prepared, each containing water-saturated ^{14}C-PBBs or ^{14}C-HCB and a fixed amount of Catlin silt loam soil. The two dosages of soil were 50 mg/L and 500 mg/L. The bottles were removed from the shaker after varying time intervals and analyzed for their ^{14}C-PBBs and ^{14}C-HCB activity. The results showed that shaking times of 3.5 and 1.5 hours were sufficient to reach equilibrium conditions for PBBs and HCB respectively. Filonow, Jacobs, and Mortland (1976), however, reported that 4 hours of shaking were needed for PBB to reach equilibrium. Thus, to ensure equilibration and for convenience of analysis, all samples were shaken overnight. Blanks were carried through all experiments to determine the adsorption of PBBs and HCB onto the surfaces of the glassware.

The amount of adsorption was determined from the difference between the initial concentration and the equilibrium concentration, multiplied by the volume of solution. A blank was subtracted and the amount adsorbed by each sample was converted to a unit basis by dividing by the weight of adsorbent.

MOBILITY STUDIES

The mobilities of PBBs and HCB were studied using the soil TLC technique, which was described by Helling and Turner (1968), and which later was the object of more intensive study by Helling (1971a, 1971b, 1971c). The adsorbent was slurried with water until it became moderately fluid, and then was applied with a spreader to a thickness of 0.5 mm onto a clean glass plate (20 cm x 20 cm) that had been washed with ethanol and acetone; this was followed by air drying. A horizontal line was scribed with a stainless steel spatula 14 cm above the base to stop solvent movement; vertical lines were scribed 2 cm apart. The ^{14}C-labeled PBBs or HCB were spotted 2 cm from the base and leached 12 cm with methanol and dioxane. For the fireMaster BP-6 mixture, the plates were leached 10.5 cm with acetone/water (1:1, and 8:2, v/v), acetone, and carbon tetrachloride. The activity of ^{14}C-labeled PBBs varied between 107,000 dpm and 214,000 dpm (3.4 µg and 6.8 µg). Ten µg of fireMaster BP-6 mixture was spotted on the soil TLC plates.

The plates were immersed in 0.5 cm of various solvents in a closed glass chamber and were removed when the solvent front reached the 12-cm or 10.5-cm line. The soil plates were removed and air dried. Soils were scraped off the plates in increments of 1 cm, starting 1.5 cm above the base of the plate. The soils were placed into 15-mL glass centrifuge tubes and moistened with 0.2 mL of ethanol/water (1:1, v/v), then extracted with three portions of 3 mL of hexane. The soil-solvent mixture was vibrated on a Deluxe Mixer (Scientific Products, McGraw Park, Illinois) for 1 minute, and

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the organic layer was decanted into a second tube.

The ^{14}C was assayed by liquid scintillation counting. One mL of the hexane extract was counted in the same way as described above. The percentages of the ^{14}C-PBBs measured in each segment were calculated based on the total ^{14}C extracted. In all studies the recoveries of PBBs and HCB from soil TLC plates were at least 96 and 91 percent, respectively. The R_f values were computed from statistical peak analysis of the data by using values of the first moment for grouped data (Hewlett-Packard, 1974).

The fireMaster BP-6 was extracted from the soil segments and the extracts were concentrated to amounts of 0.5 to 0.9 mL by using a K-D concentrator in a water bath. Concentrated extracts were analyzed on a Perkin-Elmer Sigma I gas chromatograph.

The studies of HCB mobility followed these same procedures. For the quantitation of non-^{14}C-HCBs, the hexane extracts were concentrated prior to analysis to amounts of 1 to 4 mL by gas chromatography.

In separate column leaching studies, 5 g each of 100 mesh Houghton muck soil and Catlin soil were placed into 10-mL serological pipettes. The soil columns were prewetted with 2 mL of ethanol, then percolated with 12 mL of ethanol containing 347,229 dpm ^{14}C-PBBs (11.2 µg) and 143,502 dpm ^{14}C-HCB (13.38 µg) respectively. Four mL of ethanol were added to wash the soil columns. The total ^{14}C-PBBs and ^{14}C-HCB recovered from the eluents were assayed by liquid scintillation counter.

MICROBIAL DEGRADATION STUDIES

Soil incubations

The susceptibilities of PBBs and HCB to biodegradation were evaluated using Catlin silt loam soil. Thirty grams of air-dried soil that had been passed through a 2-mm sieve was placed into 250-mL Erlenmeyer flasks. One-third of the flasks received 5 mL distilled water; 1 day later they received 3 mL of propylene oxide, which was distributed dropwise on the soil surface. The flasks were covered with aluminum foil and placed in a hood for 3 days to allow the sterilant to be volatilized. Sterilization was confirmed by inoculating a loopful of soil on a nutrient broth agar slant and finding no growth after 1 week of incubation.

Half of the nonsterilized flasks were inoculated with 5 mL of mixed culture (Clark, Chian, and Griffin, 1979), which previously had been found to degrade water-soluble PCBs. Sterilized and nonsterilized flasks received 1 mL of 300 ppm PBB solution in ethanol distributed dropwise on the soil. All flasks were sealed with a sterilized, aluminum foil-wrapped rubber stopper. Ten and five mL of sterilized, deionized water were added to nonsterilized and sterilized soil samples respectively. These samples were then incubated in the dark at 22 ± 2°C for 0, ½, 1, 2, and 6 months.

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To find the best solvent system for extracting PBBs from soil, 30 g of Catlin silt loam soil were placed in 250-mL Erlenmeyer flasks. One mL of 100-ppm PBBs was distributed on the soil surface dropwise and moistened with 10 mL of deionized water. The three solvent systems tested were 40-mL portions of hexane/acetone (9:1, v/v), benzene/isopropanol (2:1, v/v), and benzene/hexane (1:1, v/v). The results showed that hexane/acetone (9:1, v/v) yielded satisfactory recoveries of PBBs.

Three flasks of each treatment were extracted after each incubation period. PBBs were extracted from soil with 40-mL portions of hexane/acetone (9:1, v/v). This was a better extraction mixture than benzene/isopropanol because it reduced the amount of soil organic matter extracted, yet recovered as much of the PBBs. The solvent-soil mixture was shaken on a rotary shaker at 300 rpm for 30 minutes prior to decanting. Anhydrous sodium sulfate was added to the combined extracts to remove any remaining water.

The extract was concentrated to 100 mL, then 1 mL of this solution was diluted to 3 mL, with 0.75 µg of hexabromobenzene in hexane added as an internal standard. PBBs were analyzed on a Perkin-Elmer Sigma I gas chromatograph. The instrumental conditions were the same as those described in previous sections.

For the HCB incubation studies, Catlin silt loam soil was selected again. The same procedures and incubation conditions were followed as for PBBs except that 1 mL of 100-ppm HCB in ethanol was added to each flask and the soil was incubated for 0, 1, 2, and 6 months. In preliminary studies of HCB extraction from soil using different solvents, the results indicated that soil samples prewetted with water/methanol (1:1, v/v) and extracted with benzene or hexane yielded satisfactory recoveries of HCB. Benzene/isopropanol (2:1, v/v) also yielded good results in terms of HCB extraction efficiency.

The soil samples were prewetted with 10 mL of a water/methanol mixture, then extracted with three 40-mL portions of hexane because this reduced the amount of soil organic matter co-extracted with the HCB. The combined extracts were condensed to 100 mL. One mL of the extract was diluted to 3 mL with hexane, and 0.75 µg of tribromobenzene was added as the internal standard. The diluted extracts were then analyzed on a Perkin-Elmer Sigma I gas chromatograph.

Mixed culture studies

Studies were done with a mixed culture of microorganisms that had previously been isolated (Clark, Chian, and Griffin, 1979) from Hudson River sediment from the Fort Miller disposal site in New York (Leis et al., 1978). The predominant organisms found in the mixed culture were *Alkaligenes odorans*, *Alkaligenes denitrificans*, and an unidentified bacterium (Clark, Chian, and Griffin, 1979). This culture was known to degrade PCBs; we wanted to learn if the culture could metabolize HCB or any of the PBB isomers when it was in a growth mineral medium (developed by Gray and Thornton, 1928) under the same conditions as described by Clark, Chian, and Griffin (1979):

KNO_3	1.0 g/L	$FeCl_3$	0.02 g/L
$MgSO_4$	0.2 g/L	NaCl	0.1 g/L
$CaCl_2$	0.1 g/L	K_2HPO_4	1.0 g/L

The deionized water used to make up this growth medium was saturated with PBBs and/or HCB. Ten mL of a 3-day-old culture were added to 200 mL of mineral medium with PBB- and/or HCB-saturated water. The solutions were shaken at 23° ± 2°C on a rotary shaker for 0, 2, and 4 weeks. Samples without inoculum were used as controls. After the indicated periods of time, two samples of each treatment were extracted with three portions of 30 mL of water-saturated hexane. Anhydrous sodium sulfate was added to the combined extracts to remove excess water, and the extracts were concentrated to 1 mL prior to gas chromatographic analysis. The gas chromatographic conditions were explained in a previous section.

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SECTION 5

SOLUBILITY OF PBBs AND HCB IN WATERS AND LEACHATES

ISOMER IDENTIFICATION

A PBB mixture contains a variety of isomers. More than thirty isomers have been separated by using a WCOT SE-30 glass capillary column (fig. 2);

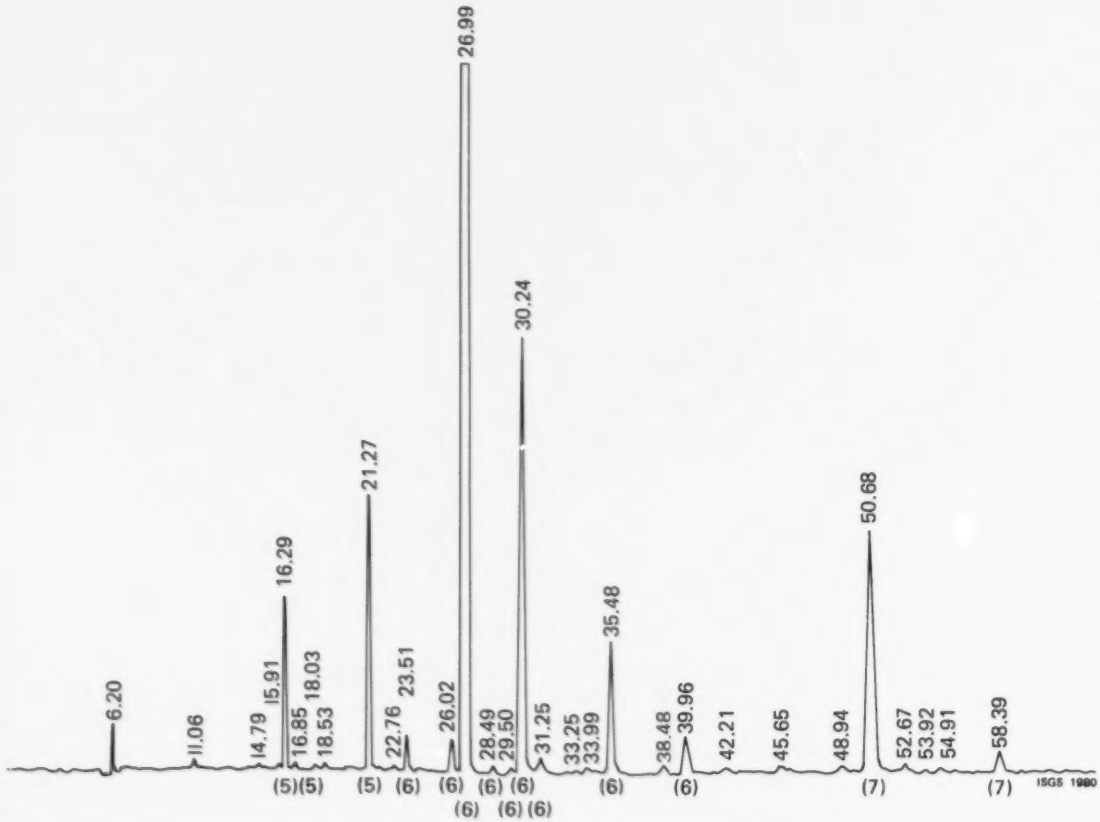

Figure 2. Gas chromatogram of PBB isomers on SE-30 WCOT glass capillary column, using ^{63}Ni electron capture detector. The numbers on each peak are the retention times in minutes; the numbers along the baseline are the numbers of Br atoms present in the particular isomer as identified by mass-spectral analysis.

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(4-76)

of these, ten major isomers were separated by using a packed 3 percent SE-30 column. Several of these major isomers have been identified: 2,2',4,5,5'-penta-; 2,3',4,4',5-penta-; 2,2',4,4',5,5'-hexa-; 2,2',3,4,4',5'-hexa-; 2,3',4,4',5,5'-hexa-; 2,2',3,4,4',5,5'-hepta-; and 2,2',3,3',4,4',5,5'-octa-brominated biphenyl (Sundström, Hutzinger, and Safe, 1976; Jacobs, Chou, and Tiedje, 1976; Dannan, Moore, and Aust, 1978). The remaining peaks were identified according to numbers of bromine atoms by mass spectrometer analysis, and the results are given in figure 3.

QUANTITATION

Because it was not possible to obtain all the individual PBB isomers, the whole PBB mixture was used for quantitation. The fireMaster BP-6 mixture was analyzed using the flame ionization detector (FID). The FID gives a

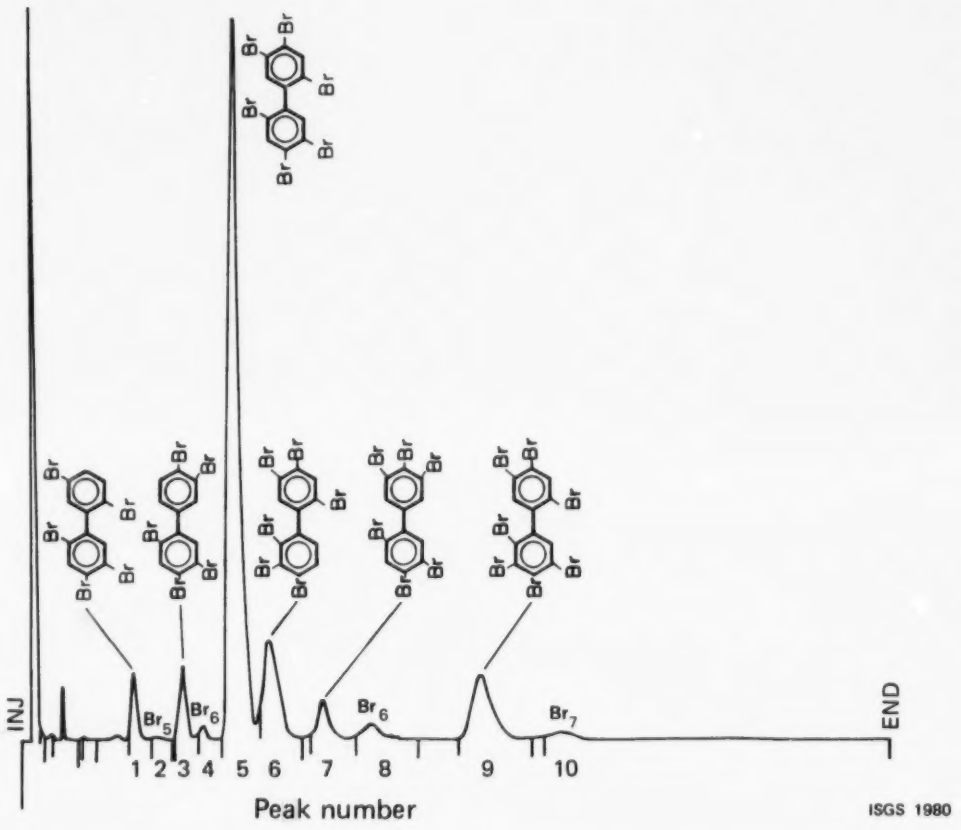

Figure 3. Gas chromatogram of the PBB mixture fireMaster BP-6 on 6-ft glass column packed with 3 percent SE-30 on 80/100 mesh Chromosorb WHP.

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nearly linear response to all the isomers of PBB, whereas the electron capture detector (ECD) gives a greater response to those isomers with higher amounts of Br atoms. An assumption was made that all of the isomers of fireMaster BP-6 produced identical FID responses, so the quantity of each isomer in a standard of known concentration was calculated from these responses. Based on the known concentration of each isomer and the added internal standard (hexabromobenzene), the relative response factors of the ECD were determined. Table 4 lists the relative responses of the ECD to the internal standard and the ten major PBB isomers. Although the responses to each isomer were not identical, they were in the same range. The only exceptions were peaks 2 and 10. Examination of figure 3, however, illustrates that peaks 2 and 10 are minor constituents in the mixture. Integration errors for these two small broad peaks are probably the reasons for the discrepancy. At any rate, even a large difference in the response factors yields only a small error in quantitation of the mixture because peaks 2 and 10 are such small components of the total mixture.

TABLE 4. THE RELATIVE RESPONSE OF A ^{63}Ni ELECTRON CAPTURE DETECTOR TO HEXABROMOBENZENE AND PBB ISOMERS; PEAK NUMBERS REFER TO FIGURE 3

Component	Relative response (µg/area)
Internal standard (hexabromobenzene)	9.933×10^{-5}
Peak 1 (5 Br)	6.801×10^{-5}
Peak 2 (5 Br)	1.360×10^{-4}
Peak 3 (5 Br)	7.096×10^{-5}
Peak 4 (6 Br)	6.337×10^{-5}
Peak 5 (6 Br)	7.598×10^{-5}
Peak 6 (6 Br)	7.995×10^{-5}
Peak 7 (6 Br)	9.750×10^{-5}
Peak 8 (6 Br)	9.920×10^{-5}
Peak 9 (7 Br)	8.712×10^{-5}
Peak 10 (7 Br)	1.160×10^{-4}

To confirm the quantitative analysis, three standard solutions were checked. Two standards containing 0.3 ppm and 0.8 ppm PBB mixtures respectively, and 0.25 ppm hexabromobenzene (internal standard) were prepared. A 1-mL volume of 1 ppm PBB standard and 10 µL of 25 ppm hexabromobenzene was added to 19 mL of hexane and then evaporated in a micro K-D condenser to approximately 1 mL. One-µL samples of the standards were injected into the gas-liquid chromatograph. The results of the analysis (shown in table 5) showed that in all cases, the overall standard deviation for the coefficient of error ranged from 2.75 to 3.76 percent. We considered this excellent for analysis in the parts-per-billion (ppb) range of concentrations.

The same technique was used for the quantitative analysis of HCB. In two separate measurements, the standard deviation of the coefficient of error for 0.03 ppm and 0.05 ppm samples of the HCB standards was less than 1 percent.

The results show that the quantitation methods developed in this study produced quite satisfactory results. By using an internal standard, the determinations of concentrations of individual PBB isomers in a mixture of isomers were relatively accurate.

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TABLE 5. COMPARISON OF CONCENTRATIONS OF PBB ISOMERS DETERMINED BY THE INTERNAL STANDARD (IS) TECHNIQUE USING AN ELECTRON CAPTURE DETECTOR (ECD) WITH THOSE RESULTS CALCULATED FROM FLAME IONIZATION DETECTOR (FID) RESPONSE DATA

Peak no.	300 ppb PBB STD		800 ppb PBB STD		1000 ppb PBB recovered from (K-D)	
	FID results (ppb)	ECD (IS)*results (ppb)	FID results (ppb)	ECD (IS) results (ppb)	FID results (ppb)	ECD (IS) results (ppb)
1	8.2	8.23	21.9	20.75	27.5	28.10
3	13.8	14.13	36.8	35.05	46.0	43.90
4	2.4	2.53	6.5	6.05	8.1	8.20
5	178.0	181.80	474.7	469.45	593.4	586.90
6	31.9	33.23	85.1	84.75	106.4	101.00
7	15.6	16.43	41.5	41.85	51.9	50.70
8	6.7	6.37	17.9	18.30	22.4	22.40
9	37.3	39.30	99.4	95.20	124.2	117.30

*Each value is a mean of 3 injections.
STD = Standard.

In other studies using the radio-labeled compounds, we obtained nearly complete recovery (complete recovery being 100 percent) of spiked PBBs and HCB when extracting from deionized water. No detectable ^{14}C was found in the ^{14}C-PBB and ^{14}C-HCB spiked aqueous samples. The percentage of recoveries of spiked PBBs and HCB that had gone through the concentration step using the Kuderna-Danish (K-D) concentrators ranged from 97.03 to 98.56 percent for PBBs and from 95.34 to 96.71 percent for HCB.

SOLUBILITY IN PURE WATERS

The major tasks in measuring the solubilities of these compounds in aqueous solutions were (1) to saturate the water with the compound by adding an excess of the compound and stirring the solution until equilibration was achieved, and (2) to separate the solid phase from the liquid phase, and then conduct a chemical analysis of the liquid phase. The greatest problem concerned the latter task—how to separate the solid from the liquid so that accurate, reliable measurements of the compound's solubility in water could be made. To solve this problem, at first we tried to centrifuge the aqueous suspension at speeds up to 20,000 rpm; however, these attempts yielded sporadic and widely varying results. The reasons were two-fold: first, some of the compound always floated on top of the aqueous layer due to the effects of surface tension; and second, it was difficult to decant or extract a sample without disturbing the solid phase because it would not compact in the bottom of the centrifuge tube and was easily disturbed and resuspended. Both these problems yielded unreliable and unacceptable data and consequently led us to

abandon centrifugation in favor of filtration as a means of separating the solid phase from the liquid.

Filtration studies

For the filtration studies, glass wool plugs, glass microfiber filters (0.7 µm), Millipore cellulose acetate membranes (0.45 and 0.22 µm), and Teflon membranes (0.5 µm) were tested to determine their effects on the solubilities of PBBs and HCB in deionized water. In all cases, the cellulose acetate membranes adsorbed the greatest amount of either PBBs or HCB and required the most presaturation. The data in figure 4 shows that continuously passing nine 100-mL portions of HCB-saturated water through the membrane saturated the adsorption sites and yielded constant and reproducible plateau values for the concentration of the compound passing through the membrane. Figure 4 also illustrates that pore size has a definite effect on the solubility value and that presaturation of the membranes by soaking in HCB-saturated water yields results that are not significantly different from results obtained by passing solution through the membrane. These data led to adoption of the presaturation technique described in the Methods Section of this report.

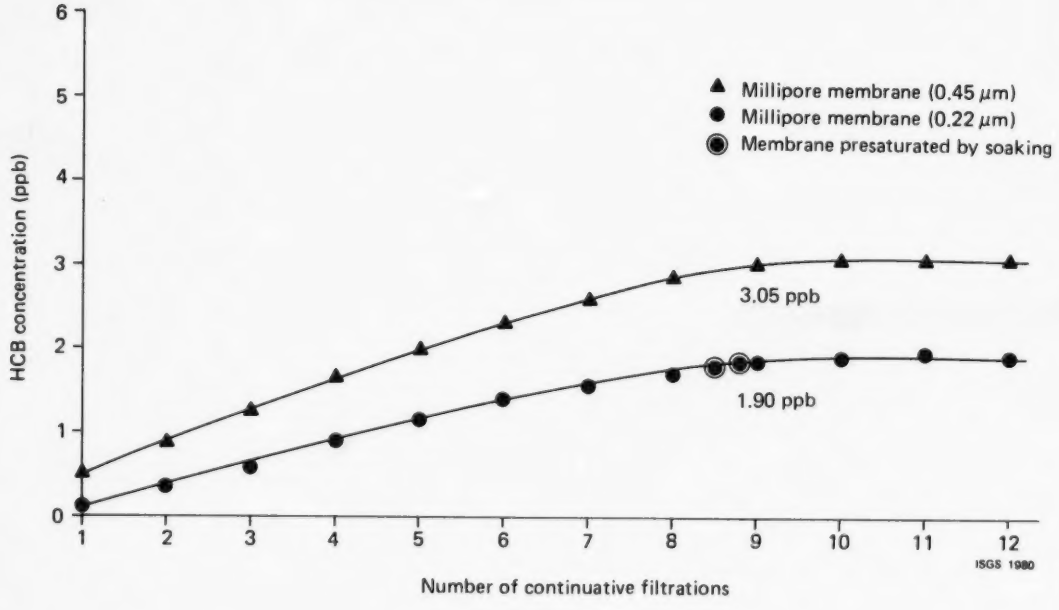

Figure 4. Effect of pore size and number of continuative filtrations of 100-mL aliquots of HCB-saturated water on the concentration of HCB in filtrates.

The compositions of penta- (peaks 1, 2, and 3), hexa-(peaks 4, 5, 6, 7, and 8), and hepta-(peaks 9 and 10) isomers in the hexane- and water-soluble fractions of fireMaster BP-6 are compared in table 6. In general, the water-soluble fractions of the PBB mixtures were richer in the lower brominated isomers than the original (hexane-soluble) PBB mixtures—this should be considered when attempting to predict PBB migration in aqueous solution.

TABLE 6. DISTRIBUTION OF PBB ISOMERS IN HEXANE- AND WATER-SOLUBLE FRACTIONS OF FIREMASTER BP-6, BASED ON TOTAL AREA*

Isomers (#Br)	Hexane-soluble (%)	Water-soluble† A (%)	Water-soluble† B (%)
1 (5 Br)	3.84	18.30	16.49
2 (5 Br)	0.31	6.06	6.31
3 (5 Br)	5.02	17.09	15.50
4 (6 Br)	1.21	3.48	4.73
5 (6 Br)	60.44	27.32	31.61
6 (6 Br)	10.42	14.92	12.00
7 (6 Br)	4.42	4.12	5.50
8 (6 Br)	1.39	1.50	1.08
9 (7 Br)	11.92	6.51	5.69
10 (7 Br)	0.91	0.70	1.10
TOTAL	99.88	100.00	100.01

*Using electron capture detector.
†PBB-saturated water filtered through glass wool (A), and glass microfiber filter (B).

The results of solubility measurements of the major isomers of PBBs in deionized water using several filter media are given in table 7. Using five different filtration media, the concentrations of PBBs ranged from 0.21 to 1.36 µg/L. A concentration of 8.32 µg/L was obtained in nonfiltered aqueous solution. Similar data on the solubility of HCB in deionized water are shown in table 8. The concentrations ranged from 1.49 to 7.69 µg/L in the five filtration studies, and a concentration of 10.09 µg/L was obtained in the nonfiltered sample. All the results were consistent and reproducible.

TABLE 7. SOLUBILITY OF THE MAJOR ISOMERS OF PBBs IN DEIONIZED WATER AS A FUNCTION OF FILTER MEDIA AT ROOM TEMPERATURE

Filtration	Concentration of PBB isomers in deionized water (µg/L)* Total	Peak 1	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
None; PBB-saturated water†	8.32	1.26	1.16	0.37	3.03	1.30	0.41	0.16	0.63
Glass wool plug	1.38	0.27	0.26	0.05	0.40	0.21	0.06	0.03	0.10
Glass microfiber filter (0.7 µm)	1.14	0.21	0.16	0.08	0.40	0.13	0.05	0.03	0.08
Millipore cellulose acetate membrane (0.45 µm)	0.77	0.11	0.09	0.04	0.31	0.10	0.03	0.03	0.06
Millipore cellulose acetate membrane (0.22 µm)	0.31	0.04	0.06	0.01	0.10	0.06	0.01	0.01	0.02
Teflon membrane (0.5 µm)	0.22	0.03	0.03	0.01	0.07	0.04	0.01	0.01	0.02

*Each value is a mean of 6 replications.
†PBB water mixture was stirred 5 months, then stood quiescent for 1 month.

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In all cases the solubilities of PBBs and HCB were very low compared with other chlorinated hydrocarbons such as PCBs, which had a solubility of 700 µg/L (Griffin and Chian, 1979). The data in tables 7 and 8 indicate a relationship between concentration and porosity of the filter medium. Concentration in the filtrate dropped in proportion to the nominal pore size of the filter material, with the exception of the Teflon membrane.

TABLE 8. SOLUBILITY OF HCB IN DEIONIZED WATER AS A FUNCTION OF FILTER MEDIA AT ROOM TEMPERATURE*

Treatment	Concentration (µg/L)†
None; HCB-saturated water	10.09
Glass wool plug	7.69
Glass microfiber filter (0.7 µm)	4.58
Millipore membrane (0.45 µm)	3.02
Millipore membrane (0.22 µm)	1.89
Teflon membrane (0.5 µm)	1.49

*After 1 year equilibration.
†Each value is mean of 5 replications.

The Teflon membrane had a nominal pore size of 0.5 µm, but consistently yielded filtrates with concentrations of one-half to one-third less than the 0.45-µm pore size cellulose acetate membrane. One reason for this could be the hydrophobic nature of the Teflon (Teflon has a bubble pressure of 15 lb/sq in.), which was needed for water to flow through the pores. We hypothesize that the effects of the surface tension of the water around the pores yield an effective pore size that is less than 0.5 µm, thus producing lower concentrations in the filtrates than did the cellulose acetate membrane of the same pore size.

The results showed that filter pore size was a major factor in the measurement of the aqueous solubility of PBBs and HCB. A finite pore size may allow particles smaller than the pore to pass through; this consequently affects the measurement of solubility. The actual solubilities may be even lower than those values reported here. Recognizing that the definition of solubility in this case is an operational one, we chose the 0.22-µm cellulose acetate membrane for future studies of solubility and adsorption measurements. This was done because we believed that the smaller pore size yielded filtrates that were more representative of the "true" solubility than the larger pore size, and because the hydrophilic cellulose acetate membranes were operationally easier to use and less costly than Teflon, while yielding comparable solubility values.

SOLUBILITY IN WATERS AND LEACHATES

The solubilities of PBBs and HCB in waters and leachates as a function of time are shown in tables 9 and 10. The results show that the solubilities of both PBBs and HCB were very low, and that there was no significant change in the measurements after 2 days, 6 months, or even 1 year. We concluded, therefore, that equilibrium was complete within 2 days.

The average solubilities of PBBs in distilled water, deionized water, creek water, Du Page leachate, and Blackwell leachate were 0.057 µg/L, 0.317 µg/L, 0.497 µg/L, 8.889 µg/L, and 16.892 µg/L, respectively, and the average solubilities of HCB in the same waters and leachates were 1.75 µg/L,

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TABLE 9. SOLUBILITY OF PBBs IN WATERS AND LEACHATES (µg/L)* FILTERED THROUGH PRESATURATED MILLIPORE MEMBRANE (0.22 µm) AS A FUNCTION OF EQUILIBRATION TIME

	Distilled water			Deionized water			
Peaks	2 days	4 days	7 days	2 days	4 days	7 days	6 months
1	BDL	BDL	BDL	0.030	0.029	0.035	0.037
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	0.040	0.038	0.045	0.055
4	0.001	0.002	0.001	BDL	BDL	BDL	0.013
5	0.035	0.032	0.038	0.136	0.142	0.125	0.100
6	0.004	0.003	0.004	0.059	0.050	0.064	0.062
7	BDL	BDL	BDL	0.017	0.016	0.015	0.014
8	BDL	BDL	BDL	0.009	0.008	0.015	0.012
9	0.017	0.019	0.016	0.028	0.025	0.026	0.023
10	BDL	BDL	BDL	BDL	BDL	BDL	BDL
TOTAL	0.057	0.056	0.059	0.319	0.308	0.325	0.316

	Sugar Creek			Du Page			Blackwell		
Peaks	2 days	4 days	7 days	2 days	4 days	7 days	2 days	4 days	7 days
1	0.038	0.034	0.043†	0.461	0.501	0.448†	0.610	0.660	0.721†
2	BDL	BDL	BDL	0.242	0.240	0.244	0.490	0.498	0.520
3	0.040	0.039	0.044	0.901	1.005	0.760	1.415	1.373	1.467
4	0.005	0.004	0.006	0.178	0.210	0.163	0.306	0.314	0.333
5	0.175	0.161	0.190	2.605	2.686	2.417	5.615	5.097	6.141
6	0.067	0.087	0.089	1.673	1.979	1.457	3.000	2.979	3.149
7	0.039	0.037	0.042	0.910	0.923	0.788	1.857	1.709	1.901
8	0.037	0.039	0.038	0.510	0.490	0.469	0.773	0.756	0.711
9	0.080	0.074	0.084	1.050	1.203	0.930	1.925	1.908	2.136
10	BDL	BDL	BDL	0.430	0.427	0.368	0.790	0.725	0.798
TOTAL	0.481	0.475	0.536	8.960	9.664	8.044	16.781	16.019	17.877

*Each value is a mean of 2 replications.
†Each value is a mean of 4 replications (2 separate sets).
BDL = Below detection limit.

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1.78 µg/L, 2.22 µg/L, 4.14 µg/L, and 4.47 µg/L, respectively. The higher solubilities of both compounds in creek water and leachates were directly correlated with the level of dissolved organics in the waters, as shown by the TOC values for the waters given in table 3. A similar finding for PBBs had also been reported elsewhere (Jacobs, Chou, and Tiedje, 1978). These results indicate that PBBs were more than 200 times and HCB more than 2.5 times more soluble in landfill leachates than in pure waters. The type of dissolved organic matter is also apparently important in determining how soluble the compound will be in a given water. These factors must be considered when predicting the migration of these compounds from waste disposal sites.

TABLE 10. SOLUBILITY OF HCB IN WATERS AND LEACHATES (µg/L) FILTERED THROUGH PRE-SATURATED MILLIPORE MEMBRANE (0.22 µm) AS A FUNCTION OF EQUILIBRATION TIME

Waters and leachates	Concentration (µg/L)*			
	2 days	7 days	30 days	1 yr
Distilled water	1.77	1.71	1.75	ND
Deionized water	1.83	1.67	1.78	1.89
Sugar Creek water	2.43	2.35	2.22	ND
Du Page leachate	4.17	4.04	4.14	ND
Blackwell leachate	4.58	4.29	4.47	ND

*Each value is a mean of 2 replications.
ND = Not determined.

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SECTION 6

ADSORPTION OF PBBs AND HCB BY SOIL MATERIALS AND AMBERSORB[R] CARBONACEOUS ADSORBENT

ADSORPTION ISOTHERM

All data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation:

$$\log \frac{x}{m} = \log K + 1/n \log C_f$$

where x = µg or ng of compound adsorbed; m = weight of adsorbent (g); C_f = equilibrium concentration of the solution (µg/mL or ng/mL); and K and $1/n$ are constants. The Freundlich adsorption constant K has been variously defined as the adsorbent capacity for the adsorbate (Adamson, 1967) and the degree or extent of adsorption (Harnaker and Thompson, 1972; Haque, 1975). The intercept of the linear plot of the Freundlich equation is equal to the value of K when C_f = 1 ($\log C_f$ = 0). The K value can be used to compare sorption of different components on various earth materials at unit concentration. The K values reported in this study are in units of µg/g at unit concentration of 1 µg/mL and are in units of ng/g at unit concentration of 1 ng/mL. The slope of the line gives 1/n and provides a rough estimate of the intensity of adsorption (Adamson, 1967); it also varies in a regular manner with the temperature of the system and the nature of the adsorbate (Freundlich, 1926).

ADSORPTION BY SOILS

The measurements of PBB adsorption on three soils from Blackwell leachate, and HCB adsorption from deionized water were plotted according to the Freundlich adsorption isotherm (figs. 5 and 6). The data for both compounds yielded linear and nearly parallel lines for each soil type tested.

Values of K and $1/n$ were obtained from the regression equations as the intercepts at a concentration of 1 ppb and the slope, respectively. These Freundlich parameters and the regression coefficient (r^2) are shown in table 11. All the

TABLE 11. FREUNDLICH PARAMETERS K (ng/g) AND 1/n, AND REGRESSION COEFFICIENT, r^2, FOR THE ADSORPTION OF PBBs AND ^{14}C-HCB ON VARIOUS SOILS FROM AQUEOUS SOLUTION

	Freundlich parameters					
	K		1/n		r^2	
Soils	PBB	HCB	PBB	HCB	PBB	HCB
Houghton muck	361	4193	1.99	1.12	0.9918	0.9985
Catlin silt loam	144	276	1.89	0.99	0.9820	0.9906
Ava silty clay loam	88	136	1.77	0.93	0.9790	0.9880

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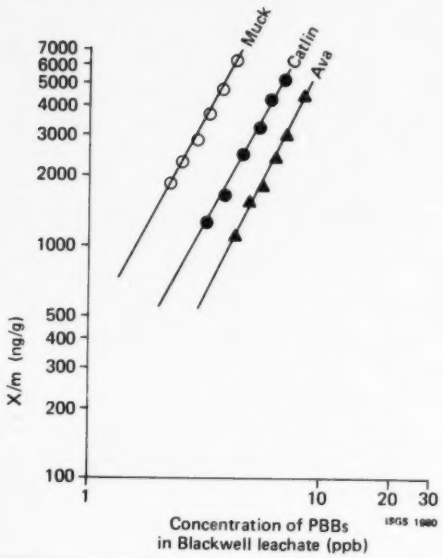

Figure 5. Freundlich adsorption isotherms of PBBs on three soil materials from Blackwell leachate at 22°C.

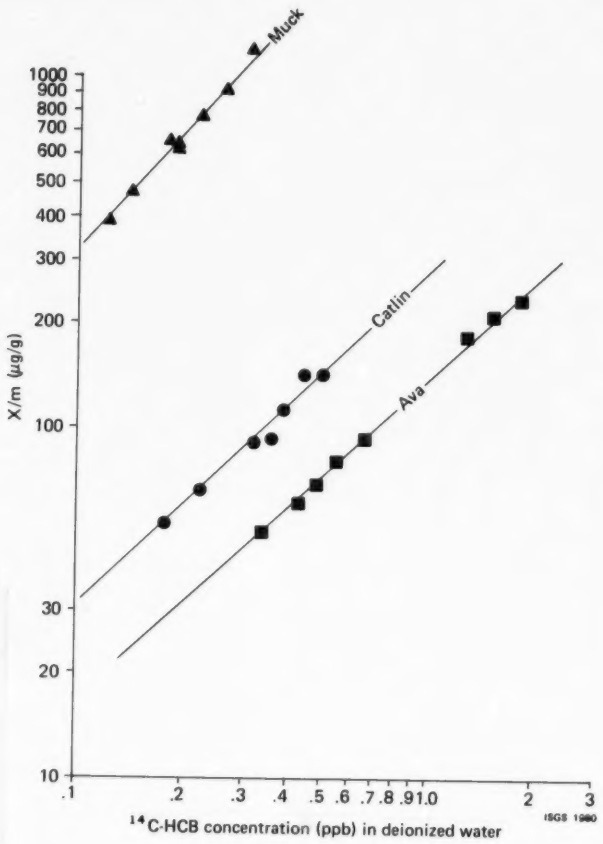

Figure 6. Freundlich adsorption isotherms of ^{14}C-HCB on three soil materials from deionized water at 22°C.

regression lines generated had coefficients (r^2) of at least 0.98, which indicate an excellent fit of the data to the Freundlich equation. The data also show that HCB had a greater tendency for adsorption on these adsorbents than did PBBs under these experimental conditions. The adsorption of PBBs and HCB on these three soils followed the series: muck > Catlin > Ava. This suggests a relationship between the organic carbon content of these soils (table 1) and their adsorption capacity for PBBs and HCB.

ADSORPTION OF INDIVIDUAL PBB ISOMERS BY SOILS

We used gas chromatogram analysis to compare the adsorptions of the major PBB isomers that were soluble in a Blackwell leachate solution by three soils. Figure 7 shows representative gas chromatograms of the Blackwell leachate-soluble PBB mixture remaining in solution after adsorption by the reaction bottle (blank) and by Catlin soil. The quantitative compositions and percentages of major PBB isomers remaining in solution after adsorption by 0.2 g of all three soils indicate that 19 percent of the leachate-soluble PBBs was adsorbed on the glass surface of the reaction bottles (table 12). Similar

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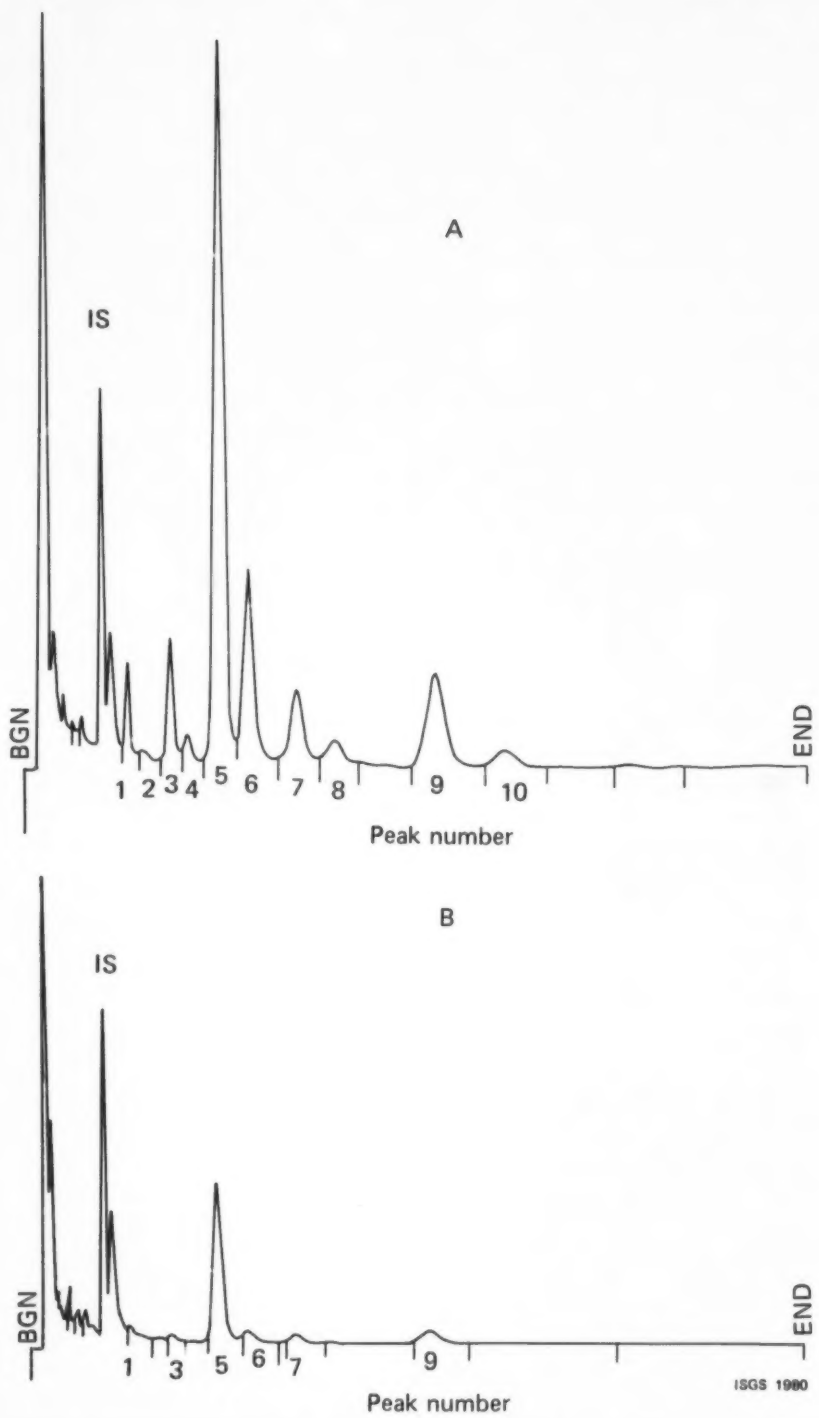

Figure 7. Gas chromatograms of PBBs remaining in Blackwell leachate (A) after adsorption on reaction bottle (blank), and (B) after adsorption by 1.2 g of Catlin soil. IS = Internal standard.

TABLE 12. QUANTITATIVE DISTRIBUTION OF MAJOR PBB ISOMERS AFTER ADSORPTION BY SOILS FROM BLACKWELL LEACHATE

Peak no.	No. of Br	Identification	Original PBB concentration (ppb)	Blank		Ava soil (0.2 g)		Catlin soil (0.2 g)		Muck soil (0.2 g)	
				(ppb)	% remaining*	(ppb)	% remaining†	(ppb)	% remaining†	(ppb)	% remaining†
1	5	2,4,5,2',5'-	0.912	0.638	74.89	0.358	52.42	0.255	37.34	0.223	32.65
3	5	2,4,5,3',4'-	1.624	1.135	69.89	0.531	46.78	0.167	14.71	0.072	6.34
5	6	2,4,5,2',4',5'-	10.177	8.337	81.92	3.744	44.91	4.244	50.91	2.989	35.85
6	6	2,3,4,2',4',5'-	3.038	2.697	88.78	1.406	52.13	0.600	22.25	0.250	9.27
7	6	2,4,5,3',4',5'-	1.766	1.489	84.31	0.682	45.80	0.475	31.90	0.221	14.84
8	6	NI	0.814	0.550	67.57	0.267	48.55	0.168	30.55	50	4.55
9	7	2,3,4,5,2',4',5'-	2.791	2.297	82.30	1.246	54.24	1.027	44.71	0.541	23.55
TOTAL			21.122	17.188	81.37	8.234	47.91	6.936	40.35	4.321	25.14

* % remaining compared with original PBB concentration.
† % remaining compared with blank.
NI = Not identified.

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findings were also observed for PCBs (Lee et al., 1979; Gresshoff, Mahanty, and Gortner, 1977).

The glass surface preferentially adsorbed peaks 3 and 8 (table 12). This preferential adsorption of individual isomers also depends on the characteristics of the adsorbent. With muck soil, which contains the highest organic matter content, peaks 3, 6, and 8 were the predominant penta-, hexa-, and hexa-bromobiphenyl peaks being adsorbed. The percentages remaining, compared with the blank, were 6, 9, and 5 percent, respectively. With Catlin soil, which lies between muck and Ava soils in organic matter content, peaks 3 and 6 were the predominant penta- and hexa-bromobiphenyl peaks being adsorbed, representing 15 and 22 percent remaining, respectively. No preferential adsorption of particular isomers by Ava soil was apparent, Ava being the soil with the lowest organic matter content. A relationship definitely exists between the organic content of the soil and the preference for adsorption by various isomers.

EFFECT OF ORGANIC SOLVENTS ON ADSORPTION BY SOILS

The adsorption of hexane- and ethanol-soluble ^{14}C-PBBs and ^{14}C-HCB by Catlin and muck soil were investigated. The results showed that little or no adsorption of either PBBs or HCB from these two organic solvents was observed. Representative data for hexane-soluble ^{14}C-PBBs and ^{14}C-HCB remaining in hexane solution after equilibrium with Catlin silt loam soil are presented in table 13.

As indicated by these results, it may not be feasible to dispose of PBBs or HCB dissolved in organic solvents on soils. A migration of PBBs and HCB from the soil surface or from a landfill environment could occur if both the PBB and HCB wastes and organic solvents were disposed of at the same location.

TABLE 13. ^{14}C-PBBs AND ^{14}C-HCB REMAINING IN HEXANE SOLUTION AFTER EQUILIBRIUM WITH CATLIN SILT LOAM SOIL AT 22° ± 1°C

Amount of soil (g)	Concentration (ppm)*	
	^{14}C-PBBs	^{14}C-HCB
0	0.325	0.227
1	0.330	0.229
2	0.324	0.227
3	0.327	0.224
4	0.320	0.224
5	0.322	0.225
6	0.323	0.223
8	0.320	0.223
10	0.322	0.225

*Each value is a mean of 2 replications. The original concentration of PBBs and HCB were 0.326 ppm and 0.228 ppm, respectively.

ADSORPTION BY AMBERSORB XE-348 FROM ORGANIC SOLVENTS

Because there was no measurable adsorption of PBBs or HCB from organic solvents by soils, the adsorption of PBBs and HCB by carbonaceous adsorbents was investigated. We wanted to learn if

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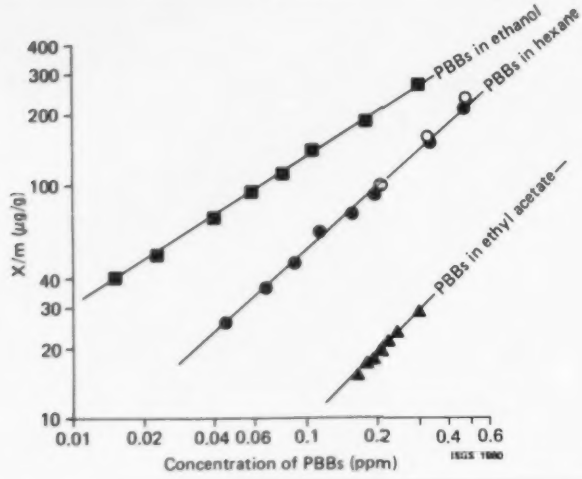

Figure 8. Freundlich adsorption isotherms of PBBs and ^{14}C-PBBs adsorption on Ambersorb XE-348 from organic solvents at 22 ± 1°C. Open symbols indicate analysis by GC.

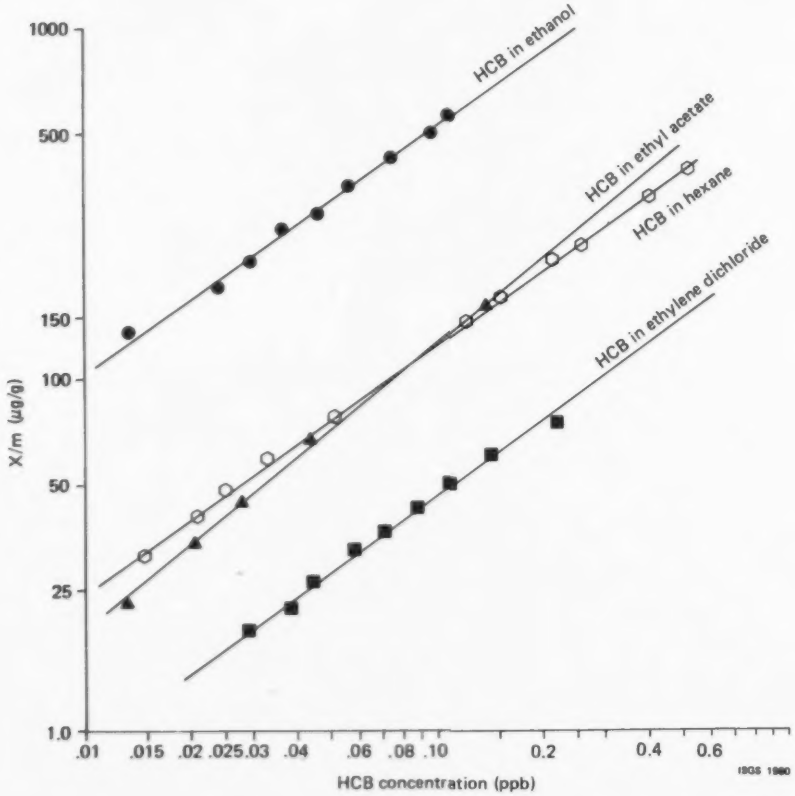

Figure 9. Freundlich adsorption isotherms of HCB adsorption from several organic solvents on Ambersorb XE-348 at 22°C.

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activated carbons or similar materials could be used to adsorb these two compounds from organic solvents.

The measurements of PBB and HCB adsorption from several organic solvents by Ambersorb XE-348 were plotted according to the Freundlich adsorption isotherm (figs. 8 and 9), and the adsorption constants and regression coefficients are given in table 14. In contrast to the results obtained with soils, these data indicate that large quantities of PBBs and HCB were adsorbed by the Ambersorb from organic solvents. There were also large differences in the amounts adsorbed among the solvents. HCB was consistently adsorbed in greater amounts than PBBs from a given solvent; this was also true for adsorption by soils from aqueous solutions.

The adsorption of individual PBB isomers by Ambersorb from hexane solution is plotted in figure 10. The preferential adsorption of the penta-bromo and hexa-bromo isomers is represented by peaks 3 and 7, and the lowest adsorption by the hexa-bromo isomer is represented by peak 4. The major component of fireMaster BP-6 is the hexa-bromo isomer, represented by peak 5, which is intermediate in adsorption. The quantity of each isomer

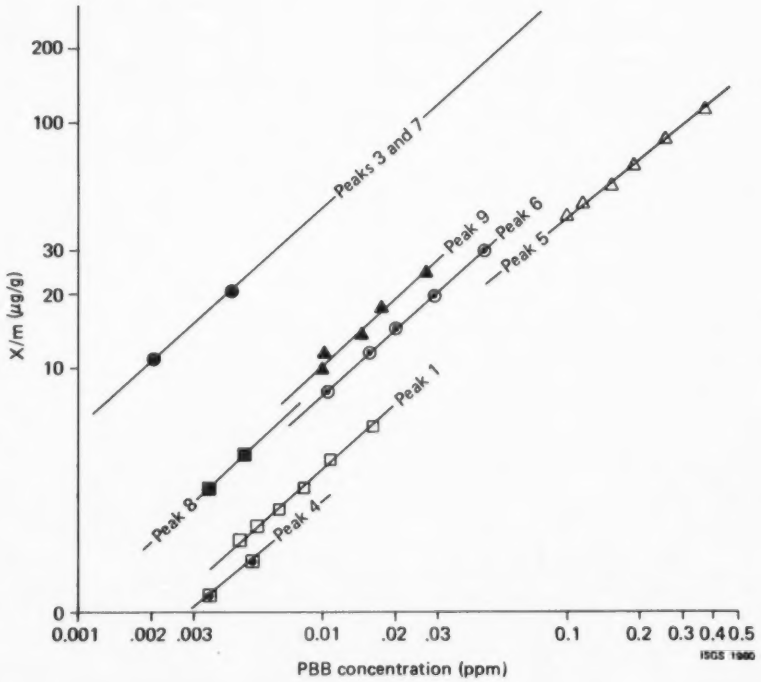

Figure 10. Freundlich adsorption isotherms of individual PBB isomers adsorbed by Ambersorb from hexane solution at 22°C.

TABLE 14. FREUNDLICH PARAMETERS K (µg/g) AND $1/n$; REGRESSION COEFFICIENT, r^2; AND MELTING POINT (M.P.), FOR THE ADSORPTION OF ^{14}C-PBBs AND ^{14}C-HCB FROM VARIOUS ORGANIC SOLVENTS BY AMBERSORB XE-348

Solvents	M. P. (°C)	Freundlich parameters					
		K		$1/n$		r^2	
		PBB	HCB	PBB	HCB	PBB	HCB
Ethanol	-114	578	2690	0.64	0.71	0.9982	0.9945
Hexane	-94	389	625	0.88	0.69	0.9995	0.9989
Ethyl acetate	-84	98	804	1.03	0.80	0.9929	0.9977
Ethylene dichloride	-36	ND	228	ND	0.70	ND	0.9924

ND = Not determined.

TABLE 15. QUANTITATIVE DISTRIBUTION OF MAJOR PBB ISOMERS REMAINING IN SOLUTION AFTER ADSORPTION BY AMBERSORB XE-348 FROM HEXANE

Peak no.	No. of Br	Identification	Blank PBB mixture (ppb)	Ambersorb XE-348			
				0.1 g		0.2 g	
				(ppb)	% remaining	(ppb)	% remaining
1	5	2,4,5,2',5'-	27.5	16.1	58.72	10.9	39.52
3	5	2,4,5,3',4'-	46.0	4.2	9.05	2.1	4.53
4	6	NI	8.1	5.1	62.42	3.4	41.75
5	6	2,4,5,2',4',5'-	593.4	368.7	62.21	25.4	42.81
6	6	2,3,4,2',4',5'-	106.4	47.1	44.26	29.1	27.34
7	6	2,4,5,3',4',5'-	51.9	0.0	0.00	0.0	0.00
8	6	NI	22.4	6.3	28.05	4.8	21.55
9	7	2,3,4,5,2',4',5'-	124.2	55.9	44.98	27.2	21.89
TOTAL			979.9	503.4	51.37	331.5	33.83

NI = Not identified.

present in the mixture and the amount adsorbed by the Ambersorb is given in table 15. The data indicate that there is no clear relationship of the quantity of isomers in the mixture, the number of bromine atoms on the molecule, and the structure of the PBB isomer to the preference for adsorption by the Ambersorb.

The adsorption capacity (K) appears to be related to the melting point of the solvents (table 14). The higher the melting point, the lower the adsorption of PBBs from the solvent. For non-ionic compounds, the higher melting point means that higher intermolecular forces, which bind these molecules to each other, must be overcome for melting to occur. This indicates,

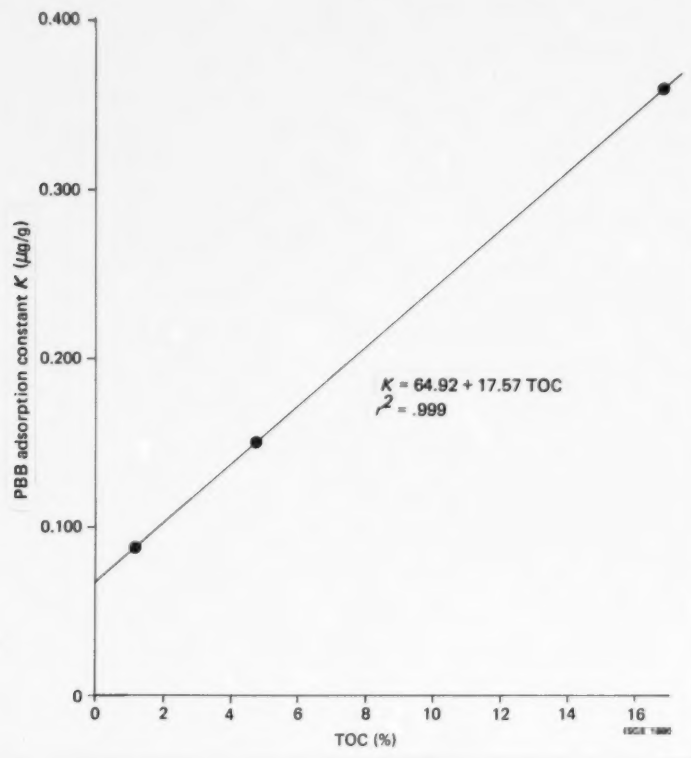

Figure 11. Freundlich adsorption constant for PBBs plotted as a function of the organic matter content of soil.

therefore, that intermolecular forces between solvent-solvent molecules and solvent-solute molecules are important factors in determining the amount of PBBs and HCB adsorbed from organic solvents.

These data, coupled with the results from soil adsorption, do indicate that the various PBB isomers have different affinities for a given adsorbent from a given solvent. These facts may be important when predicting PBB migration through soils or carbonaceous liners if the isomer distribution is markedly different than that found in fireMaster BP-6, or if various solvents are involved.

EFFECT OF SOIL TOC ON ADSORPTION

We investigated the relationship between total organic carbon (TOC) content of soil and adsorption of PBBs and HCB by soil. The PBB adsorption constant (K) was plotted as a function of TOC (fig. 11). A high correlation was found with a linear regression relation of

$$K = 64.92 + 17.57 \text{ TOC}$$

$$r^2 = 0.999$$

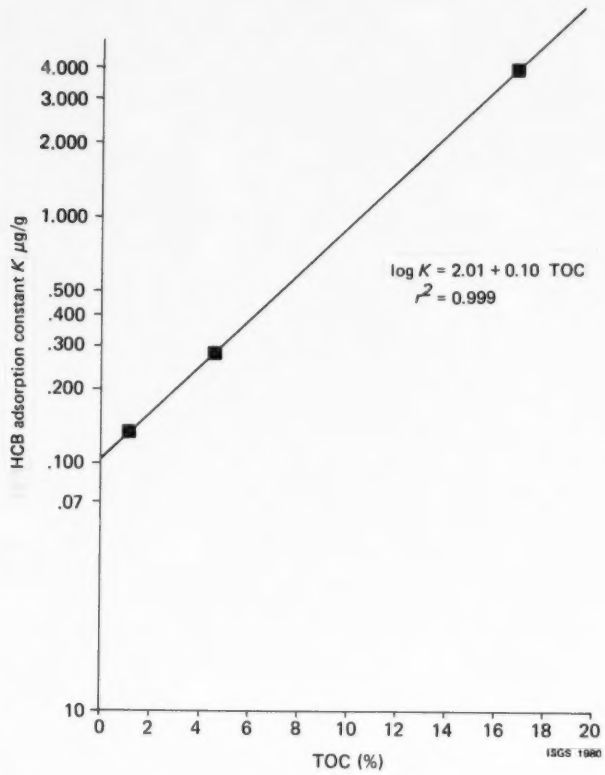

Figure 12. Freundlich adsorption constant for HCB plotted as a function of the organic matter content of soil.

A similar result was also found for HCB on the same adsorbates. Figure 12 shows the HCB adsorption constant (K) in log form plotted as a function of TOC. A high correlation was also found with a linear regression relation of

$$\log K = 2.01 + 0.10 \text{ TOC}$$

$$r^2 = 0.999$$

These results indicate that the adsorption properties of soil materials for PBBs and HCB can be predicted accurately when the TOC content of the soil is known. This information should be used with caution, however, because only three soils were used to develop the equations. The large values of the intercept indicate substantial adsorption should take place when the TOC content of the soil is zero. This implies that the mineral fraction of the soil contributed to the adsorption capacity; therefore, the relationship may be incorrect for soil materials with low TOC content.

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SECTION 7

MOBILITY OF PBBs AND HCB IN SOIL MATERIALS: DETERMINATION BY SOIL THIN-LAYER CHROMATOGRAPHY

EFFECT OF LEACHING SOLVENT AND SOIL TOC

Table 16 shows the mobilities of PBBs and HCB, expressed as R_f values, in several earth materials as determined by soil TLC measurements. The data show that PBBs and HCB remained immobile in the earth materials when leached with water and Du Page leachate, but were highly mobile when leached with organic solvents. The mobilities of PBBs and HCB in earth materials were proportional to the solubilities of the compounds in the leaching solvents, and proportional to the organic matter content of the soil, but inverse to the soil TOC content. Mobility followed this order: Ottawa sand > Bloomfield soil > Ava soil > Flanagan soil > Catlin soil. A similar finding for PCBs was reported by Griffin, Au, and Chian (1979); they also found that PCBs were extremely mobile in Catlin soil when leached with carbon tetrachloride.

PBBs and HCB are nonpolar in nature and have low solubility in water (Section 5); however, they have high solubility in organic solvents such as dioxane, carbon tetrachloride, acetone, methanol, etc. The mobilities of

TABLE 16. MOBILITY, EXPRESSED AS Rf VALUES,* OF PBBs AND HCB IN SEVERAL SOIL MATERIALS LEACHED WITH VARIOUS SOLVENTS, MEASURED BY SOIL TLC

Soil materials	Rf values*											
	Water		Du Page leachate		Acetone/water (1:1, v/v)		Methanol		Acetone		Dioxane	
	PBB	HCB	PBB	HCB	PBB	HCB	PBB	HCB	PBB	HCB	PBB	HCB
Catlin silt loam	0.00	0.00	0.00	0.00	0.01	0.00	0.40	0.40	0.69	0.45	1.00	0.99
Flanagan silty clay loam	ND	ND	0.00	0.00	ND	ND	0.60	0.44	ND	ND	1.00	1.00
Ava silty clay loam	0.00	0.00	0.00	0.00	0.02	0.01	0.61	0.48	0.76	0.80	1.00	1.00
Bloomfield loamy sand	ND	ND	0.00	0.00	ND	ND	0.86	0.72	ND	ND	1.00	1.00
Ottawa sand	0.00	0.00	0.00	0.00	0.17	0.02	1.00	0.99	0.99	1.00	1.00	1.00

*Computed from statistical peak analysis of data by using values of first moment for grouped data.
ND = Not determined.

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PBBs and HCB in earth materials were dramatically reduced when they were leached with the acetone/water mixture (table 16).

In a separate study, the mobility of the major PBB isomers was found to increase when the percentage of water decreased in the acetone/water mixtures. The results are given in tables 17, 18, and 19. We believe the same conclusion holds for the mobility of HCB in acetone/water mixtures.

COLUMN LEACHING STUDIES

Another study using soil columns also showed that no PBBs or HCB were retained in the columns when ethanol containing ^{14}C-PBBs or ^{14}C-HCB was percolated through the soil columns (table 20). These data confirmed our

TABLE 17. MOBILITY OF MAJOR PBB ISOMERS IN CATLIN SILT LOAM LEACHED WITH ACETONE/WATER (1:1, v/v)

Mobility (cm)	Distribution of PBB isomers (%)						
	Peak 1	Peak 3	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
0	85.43	92.06	95.56	93.12	98.23	96.41	97.89
1	12.39	5.36	3.89	6.01	1.62	3.33	2.08
2	2.18	2.58	0.49	0.86	0.15	0.26	0.03
3	BDL	BDL	0.06	BDL	BDL	BDL	BDL

BDL = Below detection limit.

TABLE 18. MOBILITY OF MAJOR PBB ISOMERS IN CATLIN SILT LOAM LEACHED WITH ACETONE/WATER (8:2, v/v)

Mobility (cm)	Distribution of PBB isomers (%)						
	Peak 1	Peak 3	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
0	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1	BDL	0.23	0.21	0.19	0.51	BDL	0.53
2	1.65	3.85	2.47	2.19	9.57	4.65	4.60
3	7.82	30.02	18.91	16.50	47.97	32.10	30.59
4	31.31	51.65	51.84	48.55	41.96	59.74	53.95
5	46.34	11.67	23.14	27.24	0.99	3.52	10.22
6	16.54	1.05	3.18	4.85	BDL	BDL	0.10
7	5.00	BDL	0.24	0.47	BDL	BDL	BDL
8	0.89	BDL	0.01	BDL	BDL	BDL	BDL

BDL = Below detection limit.

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previous findings on soil TCL plates; it showed that nearly 100 percent of ^{14}C-PBBs or ^{14}C-HCB were recovered from soil columns percolated with organic solvent. This data also agreed with our adsorption studies, which showed that no significant amount of organic-soluble PBBs or HCB were adsorbed on soil materials.

These facts are significant for the disposal of PBBs and HCB wastes. To prevent migration of PBBs and HCB from a landfill, PBB and HCB wastes and organic solvents should not be disposed of in the same landfill area, and neither compound should be allowed to come in contact with leaching organic solvents in soils. Nonetheless, the results from the adsorption studies indicate that carbonaceous liners may restrict the migration by removal of PBBs or HCB when dissolved in organic solvents.

TABLE 19. MOBILITY OF MAJOR PBB ISOMERS IN CATLIN SILT LOAM LEACHED WITH ACETONE (100%)

Mobility (cm)	Distribution of PBB isomers (%)						
	Peak 1	Peak 3	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
8	BDL	BDL	BDL	BDL	BDL	BDL	BDL
9	1.38	1.21	0.57	0.76	1.41	3.07	0.88
10	98.62	98.79	99.43	99.24	98.59	96.93	99.12

BDL = Below detection limit.

TABLE 20. PERCENTAGES OF ^{14}C-PBBs AND ^{14}C-HCB RECOVERED FROM SOIL COLUMNS LEACHED WITH PBB- OR HCB-ETHANOL SOLUTION

	^{14}C recovered (%)					
	1st elution* (3 pore vol)		2nd elution† (1 pore vol)		Total (4 pore vol)	
	^{14}C-PBBs	^{14}C-HCB	^{14}C-PBBs	^{14}C-HCB	^{14}C-PBBs	^{14}C-HCB
Muck soil	83.65	84.52	15.69	16.73	99.33	101.24
Catlin soil	85.37	84.58	14.97	15.54	100.34	100.12

*Soil columns prewetted with 2 mL ethanol, then percolated with 12 mL ethanol containing 347,229 dpm ^{14}C-PBBs (11.2 µg) and 143,502 dpm ^{14}C-HCB (13.38 µg), respectively, through soil columns.
†4 mL ethanol was added to flush the pore space of the soil columns.

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SECTION 8

DEGRADATION OF PBBs AND HCB IN SOIL

EXTRACTION OF PBBs AND HCB FROM SOIL

The recovery of PBBs and HCB from Catlin silt loam soil are shown in tables 21 and 22; the results show that hexane/acetone (1:1, v/v) was satisfactory for extracting PBBs from PBB-amended soil. Extraction of HCB from ^{14}C-HCB-amended soil samples that were prewetted with water/methanol (1:1, v/v), then extracted with benzene or hexane, also produced satisfactory results. Benzene/isopropanol (2:1, v/v) was also satisfactory for HCB extraction from soil. In the soil incubation study, HCB was extracted from the soil (which was prewetted with water/methanol) with three 40-mL portions of hexane, since this reduced the amount of soil organic matter extracted.

It is clear from these studies that a polar organic solvent is important in the extraction of PBBs and HCB from soil. This suggests that acetone or methanol acts as a bridge between the water film on the soil particles and the nonpolar organic extraction solvent. The polar solvent breaks the water film barrier on the soil particles, and allows transfer of the compound being extracted into the nonpolar solvent, thus yielding higher extraction efficiencies from the dual solvent system than when either solvent is used alone.

TABLE 21. PERCENTAGES OF PBB ISOMERS RECOVERED FROM CATLIN SILT LOAM SOIL (3.33 ppm ADDED BY WEIGHT)

Solvent	PBB isomers recovered (%)*						
	Peak 1	Peak 3	Peak 5	Peak 6	Peak 7	Peak 9	Mean
Hexane/acetone (9:1, v/v)	94.5	97.3	98.1	89.7	98.5	96.8	95.8
Benzene/isopropanol (2:1, v/v)	89.9	92.4	89.8	83.2	81.8	92.1	89.9
Benzene/hexane (1:1, v/v)	30.5	34.4	45.6	29.4	25.3	44.7	35.0

*Each value is a mean of 3 replications.

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SOIL INCUBATION STUDIES

The recovery of PBB components and HCB after incubation in sterilized and nonsterilized Catlin soil is shown in tables 23 and 24. The data show that PBBs and HCB persisted for 6 months in the soil, with no significant decreases in concentration due to microbial degradation. The same kind of persistence has been observed in PBB incubations with mixed cultures of microorganisms that had previously degraded water-soluble PCBs (Clark, Chian, and Griffin, 1979). The results of this study agree with previous findings for PBB degradation (Jacobs, Chou, and Tiedje, 1976; 1978).

The persistence of PBBs and HCB is also consistent with evidence concerning PCBs that show that the more heavily chlorinated isomers (penta or greater) were resistant to degradation, whereas many of the lesser chlorinated components were metabolized (Ahmed and Focht, 1973; Baxter et al., 1975; Tucker, Saeger, and Hicks, 1975; Clark, Chian, and Griffin, 1979). Of interest is the loss of extractability with time of all PBB isomers (table 23) and HCB (table 24), in the sterile as well as the nonsterile treatments. This loss of extractability from soil could be due to sorption, masking, or volatilization during long term incubations. HCB is more volatile than PBB, and more HCB was lost than PBB; therefore, volatilization was probably the mechanism of loss.

We examined the fate of photodegraded PBBs because the higher brominated forms are readily degraded by ultraviolet light to lesser brominated forms that could be more toxic. It can be reasoned that the PBBs on PBB-amended soil surfaces might be subject to some photodegradation; however, this does not appear to have been a significant reaction in the long term incubation studies reported here, because the ratios of peak numbers 1:5:9 found in most of the PBB-amended soil extracts were 5.3:100:18.5, and did not vary significantly from the PBB standard (5.3:100:18.6).

TABLE 22. EXTRACTION OF ^{14}C-HCB FROM SOIL USING DIFFERENT SOLVENTS*

Hexane/acetone (%)	Benzene/isop (%)	Hexane (M/W) (%)	Benzene (M/W) (%)	Hexane (%)	Benzene (%)	Hexane/benzene (%)
77.16 (75.32)†	99.55 (97.22)	91.63 (90.32)	97.05 (95.61)	20.59	25.63	21.15
80.47 (79.01)	96.41 (93.55)	90.04 (89.40)	97.75 (96.05)	19.79	26.25	20.40
80.43 (78.46)	99.24 (96.78)	93.26 (91.25)	96.39 (94.70)	20.17	26.39	20.47

*Hexane/acetone (9:1, v/v); benzene/isopropanol (2:1, v/v); hexane/benzene (1:1, v/v); 10 mL methanol/water (1:1, v/v) was added to hexane (M/W) and benzene (M/W).
†Determined by gas chromatography.

TABLE 23. PERCENT RECOVERY OF PBB ISOMERS AFTER INCUBATION OF 10 ppm BY WEIGHT IN CATLIN SOIL*

	Incubation time				
	0 month	½ month	1 month	2 months	6 months
Peak 1					
S	82.1	80.9	79.5	73.4	73.1
N-S	83.2	80.4	80.0	74.5	75.3
I	83.7	81.5	81.7	76.1	74.2
Peak 3					
S	84.5	81.3	79.8	74.3	73.2
N-S	85.3	85.5	81.3	75.0	75.4
I	84.6	87.5	81.5	75.9	75.6
Peak 4					
S	89.5	80.3	81.0	80.4	79.3
N-S	91.3	87.7	84.8	86.1	86.8
I	90.5	88.1	86.8	88.3	85.7
Peak 5					
S	91.2	84.9	83.3	81.9	80.5
N-S	93.8	88.9	87.8	84.5	83.0
I	92.5	86.9	85.4	84.0	83.3
Peak 6					
S	89.9	85.1	84.0	82.5	81.9
N-S	92.9	89.8	88.7	84.3	83.1
I	90.4	86.1	84.5	82.3	82.8
Peak 7					
S	91.7	86.9	84.7	82.9	80.9
N-S	93.1	88.4	84.0	83.6	84.0
I	94.2	89.5	87.7	85.9	84.3
Peak 8					
S	90.8	85.3	84.1	82.0	83.0
N-S	91.6	87.9	86.6	86.4	87.2
I	92.5	88.3	87.1	86.2	86.4
Peak 9					
S	91.9	87.7	87.8	85.6	84.7
N-S	94.1	89.1	89.7	86.8	84.7
I	93.3	88.4	91.9	87.4	85.1

*Each value is the mean of 3 replications.
S = Sterilized soil.
N-S = Nonsterilized soil.
I = Inoculated mixed culture.

TABLE 24. PERCENTAGE OF HCB RECOVERED AFTER INCUBATION OF 3.33 ppm BY WEIGHT IN CATLIN SOIL

Treatment	HCB remaining in soil (%)			
	0 month	1 month	2 months	6 months
Sterilized	85.68*	82.78	79.75	63.26
Nonsterilized	89.04	84.08	82.24	64.74

*Each value is a mean of 3 replications.

In the mixed culture studies, no PBB metabolites were found in the PBB-saturated mineral solution after 4 weeks of incubation. Apparently these mixed cultures cannot degrade FireMaster BP-6. As with PCBs, the high degree of halogen substitution probably accounts for the lack of degradation.

Since PBBs are not degraded, are not leached by water (see Section 7), are not taken up by plants (Chou et al., 1978), and are not readily volatilized (because of their low vapor pressures), we expect PBBs to be a permanent component of contaminated soils. HCB also is not degraded or leached by water and is probably not taken up by plants; however, HCB has a moderate vapor pressure and its most likely path for redistribution or migration in soils is by vapor phase transport.

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APPENDIX

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